LXXXVII. *Investigation of the Orientations in Thin Evaporated Metallic Films by the Method of Electron Diffraction. By* K. R. DIXIT *.

[Plate XXXIII.]

Introduction.

VARIOUS attempts † have been made to study the structure of thin metallic films both by X-rays and electrons. The films were beaten leaves, evaporated or sputtered films. Here nobody appears to have obtained any evidence of different orientations with the same metal.

Professor Thomson, Murison, and Stuart ‡, observed different orientations with sputtered platinum films. These orientations are more or less spontaneous, there being no observable correlation between the nature of the base and orientation either in the frequency with which

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* Communicated by Prof. G. P. Thomson, M.A., F.R.S.

† Bragg, ' Nature,' cxiii. p. 639 (1924); Ingersoll and Sordahl, Phys. Rev. xxxii. p. 649 (1928); Ingersoll and Hannwalt, Phys. Rev. xxxiv. p. 972 (1929); Dembinska, *Zeit. f. Phys.* liv. p. 46 (1929); *Acad. Polonaise sci. et lettres*, Bull. 9–10, p. 460 (1930); E. Rupp, *Ann. der Physik*, i. p. 801 (1929); Trillat and Hirsch, *C. R.* cxciii. p. 649 (1931); *C. R.* cxciv. p. 72 (1932); *J. de Phys.* cxi. p. 195 (1932); *Zeit. f. Phys.* lxxv. p. 784 (1932); Kirchner, *Zeit. f. Phys.* lxxvi. p. 576 (1932); Finch and Quarrel, ' Nature,' cxxxi. p. 877 (June 1933).

‡ Prof. Thomson, Murison, and Stuart, Proc. Lond. Phys. Soc. xlv. p. 381 (May 1933).

the orientation occurred or in the preferred plane. It is doubtful also if the nature of the gas has any marked effect on the types of orientation. The suggestion is advanced that the orientation—itself a comparatively rare phenomenon—is a thermal effect produced during or after the deposition of platinum.

The present work was undertaken at the suggestion of Prof. Thomson to find chiefly the effect of temperature on the orientations. As the evaporated * films have been observed to contain invariably less gas than the sputtered films even under the same conditions, the method employed was to evaporate the films in vacuum, to heat treat them in vacuum, and to examine the structure by electron diffraction.

The films, 10^{-4}–10^{-6} cm. thick, of silver on molybdenum, quartz, and glass, of aluminium on molybdenum, and of zinc on molybdenum, have been studied over the whole range between room temperature and boiling-point. Different orientations have been observed which do not depend on the nature of the base. A theory is proposed that these thin deposits behave as a two-dimensional gas.

The experimental apparatus consists of two parts :—

(1) Heating system.

(2) Electron camera †.

The Evaporating System.

The evaporation was done in a transparent silica tube, 25 cm. long and of 2·5 cm. internal diameter (fig. 1). It had a sealed bottom, and was closed on the top by a ground silica stopper, into which was fused a silica tube of 8 mm. bore, which served to evacuate the system and to carry the bases on to which the metals were deposited. The portion of this fused tube below the stopper had ten holes in it. The blocks used as bases were held in platinum claws, which could be hooked by platinum silver wires into the holes in the fused tube at any desired level. The metal to be evaporated was placed in a molybdenum crucible at the bottom of the large tube.

The heating was done in an electric furnace wound with nichrome wire. The temperature was recorded by a platinum-rhodium thermocouple, in conjunction with a

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* Ingersoll and Sordahl, *loc. cit.*

† Thomson and Fraser, Proc. Roy. Soc. A, cxxviii. p. 641 (1930).

millivoltmeter, and could be controlled to within 5° C. by regulating the current.

The receiving block could be maintained at any desired temperature by adjusting the position of the water-jacket relative to the block ; this was an ordinary bandage wrapped tightly round the tube and kept wet. This proved a simple and very efficient arrangement.

The annealing was done by keeping the block in a uniform temperature enclosure. The furnace could be raised and lowered by chains, while the silica tube itself could be moved vertically when under vacuum by two

Fig. 1.

A   SILICA TUBE

B   DISCHARGE TUBE

C,D   GROUND GLASS JOINTS

P   TO THE PUMPS
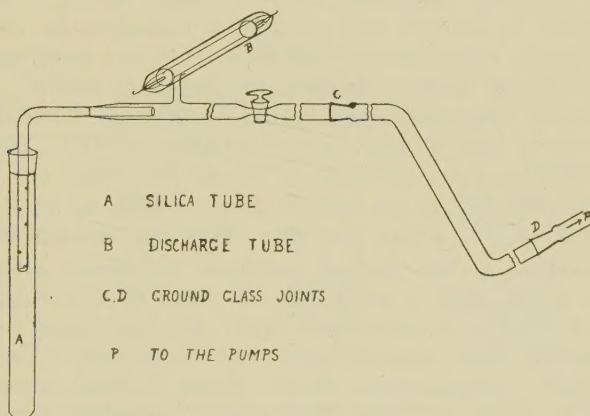
Evaporating system.

horizontal ground-glass joints at right angles to one another.

Silver.

Silver deposited on molybdenum disks at room temperatures shows complete rings of normal silver provided the mean thickness of the films is not greater than 10^{-4} cm. As reflexion of electrons was used to examine the structures even the most complete rings are semicircles. With larger thicknesses the surface of the deposit becomes irregular and the diffuse scattering is far more pronounced than the regular scattering. Even very thin films, thin enough so that rings due to polished * molybdenum

* R. C. French, Proc. Roy. Soc. A, cxl. p. 637 (1933).

besides the normal silver ones can be seen, gave complete rings.   In the case of very thin films the crystal size is naturally smaller and the rings become broader.

The thickness of the films—10^{-4} cm.—was determined by weighing, while in the case of thinner films an upper limit was found to the thickness by the depth of focus method with a very high power microscope.   The thinner films were all transparent.

Thick Films ($\sim 10^{-4}$ cm.).

The bases, which were polished molybdenum blocks, were carefully degassed.   Silver (M.p. 960° C.) layers appeared to boil off and produce a considerable surface irregularity when heated after deposition to a temperature of 800° C. or more.   Heating the layer at 940° C. gave two broad rings corresponding to the random distribution of atoms[*].   Layers kept for ten minutes at 800° C., 850° C., and 900° C., gave patterns in which the rings are very diffuse and appear to run in groups, such as $(\sqrt{3}\sqrt{4})$, $(\sqrt{8}\sqrt{11}\sqrt{12})$, $(\sqrt{19}\sqrt{20}\sqrt{24})$.   This may be due to the irregularity in the surface, perhaps combined with the effect of an inner [†] potential.   It may be that here we have a layer of super-cooled liquid, the base being cooled so quickly that crystals could not be formed.   Heating at lower temperatures either shows normal complete rings of silver or rings with spots, indicating that the crystallites have increased in size or a recrystallization has taken place (fig. 2).   These results are summarized in Table II., where the first column gives the temperatures at which the block was maintained for 10–15 minutes after the layer of silver had been deposited on to it.

Heating these thick films for a very long time appeared to produce orientations.   For instance, maintaining at 650° C. for one to three hours produced (111) orientation, indicating that a large number of small crystals are so orientated that this plane is parallel to the underlying surface.   Heating at 550° C. for one hour also produces (111) orientation, but even after heating for two hours at 400° C. complete rings are still seen.

* Wierl, *Ann. der Physik*, viii. p. 521 (1931).
† Germer, Phys. Rev. (May 1st, 1933).

Thin Films.

Very thin transparent deposits of silver on molybdenum were similarly examined after being kept at a specified temperature (column 1, Table III.) for ten minutes. The orientations were produced much more easily with thinner films. The results are given in Table III. The positions of the maximum intensity of the rings as seen on the plates are compared with those calculated on the assumption that a particular plane is parallel to the surface. A fairly good agreement is obtained, as is seen in Table I., for (111) plane of silver. When such an agreement is obtained the plane must be nearly parallel to the underlying surface. The angle between the

TABLE I.

(111) Orientation for Silver, kept at 650° C.
The Plane of Incidence taken as 0.

Ring.	Maxima observed.	Maxima calculated.
$\sqrt{3}$	0	
$\sqrt{4}$	54°, 55°	54° 43′
$\sqrt{8}$	35°, 36°	35° 20′
$\sqrt{11}$	24°, 25°	24° 30°
$\sqrt{12}$	0	0

maxima of the rings is equal to the angle between the corresponding planes for any particular orientation *. The ring corresponding to the plane which is parallel to the base is strong in the centre.

Normally any complete ring is most intense in the centre, and gradually becomes weaker as we approach towards the ends, due to the absorption of the electron waves inside the target. The effect of orientation is to increase this contrast.

The extent of orientation varies very much, from cases where the rings are reduced to isolated spots to others in which there is only a perceptible difference of intensity along the circumference, while in some cases the orientation can be observed as a modification of the relative

* Prof. Thomson, Murison, and Stuart, *loc. cit.*

normal intensities of the rings or by a few rings being absent which should be normally present. Deposition on the blocks when it is maintained at an elevated temperature appeared to show the same effect as depositing and then raising the block to that temperature.

Similar results were obtained with silver deposited on quartz, both in the case of thick and thin films

TABLE II.

Heat Treatment of Silver Films 10^{-4} cm. on Molybdenum

Temperature.	Number of specimens.	Number of plates.	Result.
940° C.	1	2	Perfectly random distribution.
900° C.	1	3	Diffuse rings, adjacent rings merge into one another.
850° C.	1	3	
800° C.	2	5	
750° C.	2	6	Complete normal rings of polycrystalline structure.
700° C.	2	5	Rings with spots (recrystallization).
650° C.	3	7	Rings with spots (best recrystallization).
600° C.	2	4	Rings with spots (recrystallization).
550° C.	2	5	Complete normal rings.
500° C.	2	4	,, ,,
450° C.	1	2	,, ,,
400° C.	1	2	,, ,,
350° C.	1	2	,, ,,
300° C.	1	2	,, ,,

investigated between 450° C. and 750° C. at 100° C. intervals.

In the case of an optically flat piece of glass it was not possible to heat the block beyond 400° C., and no heat orientation of the rings was observed.

Two mirrors of silver on glass made by Dr. Tolansky were examined. In making these mirrors for spectroscopic work silver is evaporated on to a piece of glass optically flat in a very high vacuum by using a tungsten

spiral crucible, the block being about 30 cm. away from the spiral, so that a uniform deposit is obtained. An ordinary deposited layer shows normal silver rings, rather broad, due to the smallness of the crystals. In order to make this thin layer of silver adhere strongly to glass and to increase the reflecting power these mirrors are treated with aqua-regia vapour for a minute. The layer so treated shows a mixture of Ag and Ag_2O with a large number of crystals of Ag_2O so orientated that (110) plane is parallel to the surface.

TABLE III.

Heat Treatment of Thin Silver Films 10^{-5}–10^{-6} cm. on Molybdenum.

Temperature.	Number of specimens.	Number of plates.	Result.
450° C.	1	3	Normal complete rings.
500° C.	2	6	,, ,,
550° C.	2	5	(111) orientation.
600° C.	3	8	,, ,,
650° C.	4	12	All plates showed very strong (111) orientation.
700° C.	3	7	A few showed slight (111) orientation.
750° C.	2	4	(200, 111) orientations a trace.
800° C.	2	5	Both (200, 111) rings equally strong.

Aluminium.

Thin films of aluminium 10^{-5}–10^{-6} cm. deposited on molybdenum were heat treated and the structure examined. Normal complete rings of aluminium are seen when the temperature of the base is less than 100° C. Aluminium oxidizes fairly rapidly, and care had to be taken to expose the surface to the air as little as possible. The deposit must be heat treated without exposing it to the atmosphere ; consequently the molybdenum disk had to be kept during deposition in a position which was best suited for subsequent heat treatment ; in this position the temperature of the block during deposition was 220° C.,

and when the block is at this temperature the deposited layer shows (111) orientation. This layer was heat treated, maintaining it at the temperature given in column 1, Table IV. for five to fifteen minutes, and different orientations were observed. This means that the initial orientation was destroyed and reorientation took place.

One specimen was made at each of the temperatures in column 1, and three plates were taken with every one of them.

TABLE IV.

Aluminium Films on Molybdenum, 10^{-5}–10^{-6} cm.

Temperature.	Results.
10° C.	Complete rings.
100° C.	,, ,,
160° C.	Trace of (111) orientation.
220° C.	,, ,,
260° C.	,, ,, (strong).
300° C.	This layer was rather thick, 5×10^{-5}; (111) orientation, trace of (100) orientation and recrystallization.
350° C.	(100) orientation and recrystallization.
500° C.	Trace of (100) orientation and (110) orientation.
606° C.	(110) orientation.

Zinc.

Zinc oxidizes nearly as rapidly as aluminium, and should be exposed to the atmosphere as little as possible. A thin layer, 10^{-6} cm., of zinc deposited on the molybdenum disk at a temperature of 10° C. showed orientation. All further orientations were observed by maintaining the base at some specified temperature and depositing a thin layer on to it. The results are given in Table V., where column 1 gives the temperature of the receiving block. One specimen was made at each of the temperatures in column 1, and three plates were taken with every specimen. In Table VI. a comparison is made with the X-ray spacings.

TABLE V.

Zinc deposited on Molybdenum, 10^{-5}–10^{-6} cm.

Temperature.	Result.
10° C.	(101) orientation (fig. 3).
60° C.	(102) orientation.
100° C.	Two diffuse rings strong in the centre; (101, 102, 103, 110) orientations ?
150° C.	Four broad rings, faint rings outside these broad rings, one of the broad rings very strong in the centre; (103, 110) orientation.
200° C.	Complete rings of zinc, three strong in the centre; (103, 110, 112, 201, 203, 105, 114) orientations ?
250° C.	Nearly the same as 200° C.
300° C.	(203) orientation (fig. 4).

TABLE VI.

Zinc deposited on Molybdenum (10° C.).

Ring.	Spacings with electrons in A°.	Spacings with X-rays in A°.
001 (2)	2·46	2·46
100	2·31	2·30
101	2·08	2·08
102	1·66	1·68
103, 110	1·32	1·33
	1·20	1·20
	1·13	1·13
	1·08	1·09
	1·03	1·04
	0·92	0·92
	0·87	0·85
	0·75	0·76

Theory of Orientations.

It is observed with the thin metal deposits obtained with molecular rays that the atoms after striking the target do not remain in one fixed position even if the temperature of the target is well below the transition temperature necessary for the formation of a permanent

deposit, but that they move about at random on the surface, as observed by Eastermann for silver and cadmium *.

Now the thin metallic deposits we are considering are at elevated temperatures, and there would certainly be a tendency for the atoms to move about. This layer of adsorbed atoms in random lateral motion present on a solid surface may be represented as a two-dimensional gas. We then may assume that it obeys an equation of state analogous to that of Van der Waals' for a three-dimensional gas,

$$\left(\pi_1 + \frac{\alpha}{W^2}\right)(W - \beta) = RT, \quad . \quad . \quad . \quad . \quad (1)$$

where

π_1 is the two-dimensional pressure, *i. e.*, the force per unit length of the boundary,

α and β are equivalent to Van de Waals' a and b,

W is the area of the surface on which is adsorbed one molecule,

T the temperature of the surface.

In the following discussion we will confine our attention to the first layer of atoms deposited on the surface. If by any means this layer assumes any special orientation the atoms in the superimposed layers, which are free to move about in their own planes, will have a tendency to assume the orientation of the underlying layer. The closer any layer is to the orientated layer the greater will be the tendency of the atoms to take the positions corresponding to those of the atoms in the orientated layer.

We have assumed that the first layer of atoms deposited on a polished surface behaves as a two-dimensional gas and obeys an equation similar to that of Van der Waals'. According to Van der Waals † the perfect gas equation $pv = NRT$ must be corrected in two ways. The first correction is a correction to be applied to the term v to represent the finite size of the molecules, and the second is a correction to be applied to the term p to represent the influence upon pressure of the forces of cohesion in the gas.

* Eastermann, *Zeit. Physik. Chem.* cvi. p. 403 (1923).
† Jeans 'Dynamical Theory of Gases,' p. 125 (Cambridge, 1925).

Here we are dealing with solids deposited on mechanically flattened surfaces, which cannot have a regularity of more than 10^{-6} cm., which is more than ten times the atomic diameter. In the case of any atom in the first layer of the deposit its centre can lie anywhere in this layer, as it can push the other atom slightly away from the surface, forming a sort of arch on the base, the height of this arch not exceeding about two atoms. For mechanically polished bases, which are irregular to the extent of ten atoms at least, we may suppose that this arch still forms a part of the surface. This supposition that the arch forms a part of the base would not be correct if the irregularities in the base are regular or periodic; but the mechanical act of polishing successively in directions at right angles to one another is likely to leave small projections here and there, and the irregularities would not be periodic. Even the most flat deposit on such a surface will have to arch up. With this possibility of arching up an atom can be supposed to lie anywhere in the layer, and a correction corresponding to Van der Waals' volume correction would be unnecessary.

In Van der Waals' equation we correct the observed pressure p for the attraction between the molecules, and substitute the corrected term in the simple gas equation. In our case the observed pressure is $-\gamma$, where γ is the surface tension. The error in sign has arisen through the unfortunate practice of regarding surface tension as a physical pull parallel to the surface instead of as a mathematical fiction for free surface energy. The quantity to be substituted in the place of pressure in the simple gas equation is therefore $\pi = \gamma_0 - \gamma$, where γ_0 is a constant. Thus we see that the first layer of atoms in contact with the surface of the block obeys an equation

$$\pi A = RT, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where π is the two dimensional pressure,

    A is the area per adsorbed molecule,

    T the temperature of the surface,

    R the gas constant $8 \cdot 3 \times 10^7$ ergs/gm. deg.

If we know π or γ, then from equation (2) we can find A in terms of T. To determine π we make use of Ramsay and Shields' equation. Now Ramsay and Shields' equa-

tion for the variation of surface tension with temperature
is

$$\gamma = \frac{k(T_c - T - 6)}{(M_v)^{2/3}}, \quad \ldots \quad (3)$$

where M_v is the molecular volume, T_c is the critical
temperature, while k is the temperature coefficient of
$(M_v)^{2/3}$, a quantity called "molecular free surface energy."
The quantity k is constant for a great number of normal
liquids and has a mean value $2 \cdot 1$, even in the most abnormal
cases $k \not> 20$.

It is justifiable to use Ramsay and Shields' equation for
the layer we are considering, because although the layer
is gaseous if we consider the mobility, it is solid or liquid
from density considerations.

Using the relation $\pi = (\gamma_0 - \gamma)$ and equation (3), equa-
tion (2) becomes

$$\left\{ \gamma_0 - \frac{k(T_c - T - 6)}{(M_v)^{2/3}} \right\} A = RT; \quad \ldots \quad (4)$$

substituting

$$\left\{ \gamma_0 - \frac{k(T_c - 6)}{(M_v)^{2/3}} \right\} = K_2,$$

and $\dfrac{k}{(M_v)^{2/3}} = K_1$ we get for the required relation from
which we may find the value of A at any temperature T_1,

$$\frac{K_2 A}{R - K_1 A} = T. \quad \ldots \quad \ldots \quad (5)$$

In the case of silver or any other face-centred lattice
side a,

$$\text{in (100) plane} \quad A = \frac{a^2}{2},$$

$$\text{in (110) plane} \quad A = \frac{a^2}{\sqrt{2}},$$

$$\text{in (111) plane} \quad A = \frac{a^2 \sqrt{3}}{4}.$$

Substituting these values of A in (5) we get

$$T_{100} = \frac{K_2 a^2 / 2}{R - K_1 a^2 / 2}, \qquad T_{111} = \frac{K_2 a^2 \sqrt{3} / 4}{R - K_1 a^2 \sqrt{3} / 4};$$

$$\therefore \quad \frac{T_{100}}{T_{111}} = \frac{2}{\sqrt{3}} \left\{ 1 + \frac{K_1 a^2 (2 - \sqrt{3})}{4R - 2K_1 a^2} \right\}. \quad \ldots \quad (6)$$

But $K_1 a^2 = \dfrac{ka^2}{(M_v)^{2/3}}$, and here $a^2 \sim (M_v)^{2/3}$ and $K \gtrless 20$.

We may suppose $R \gg K_1 a^2$, which will be reasonable, as $R \sim 80 \times 10^7$.

$$\therefore \qquad \frac{T_{100}}{T_{111}} = \frac{2}{\sqrt{3}} = \frac{\sqrt{4}}{\sqrt{3}} = \frac{a/\sqrt{3}}{a/\sqrt{4}}, \quad \cdots \quad (7)$$

i. e., the temperatures are inversely proportional to the Bragg *d*'s for these planes.

Similarly

$$\frac{T_{110}}{T_{111}} = \frac{K_2 a^2/\sqrt{2}}{R - K_1 a^2/\sqrt{2}} \frac{R - K_1 a^2 \sqrt{3}/4}{K_2 a^2 \sqrt{3}/4}$$

$$= \frac{4}{\sqrt{2}\sqrt{3}} = \frac{\sqrt{8}}{\sqrt{3}} = \frac{a/\sqrt{3}}{a/\sqrt{8}}, \quad \cdots \quad (8)$$

neglecting $K_1 a^2$ in comparison with R, as before, which is again inversely proportional to the Bragg d for these planes.

The equations (7) and (8) can be expressed in an alternative way:

$$\frac{T_{100}}{T_{111}} = \frac{a^2/2}{a^2\sqrt{3}/4} \quad \text{and} \quad \frac{T_{110}}{T_{111}} = \frac{a^2/\sqrt{2}}{a^2\sqrt{3}/4}, \quad \cdot \quad (9)$$

that is, the temperature at which any orientation should occur is directly proportional to the area A per atom in this plane. In general if atoms are arranged in a crystal lattice the area per atom in any plane A must be inversely proportional to the perpendicular distance between the planes of that family, as is clearly seen by density considerations.

Thus the ratio of the temperatures at which orientations parallel to any planes occur can also be expressed as the inverse ratio of the perpendicular distances between the planes of that family.

Now crystals are characterized by a definite melting-point at which the crystal structure is destroyed and the atoms are capable of moving in any direction. It seems natural to suppose that the temperature at which this atomic distribution can occur is characterized by the atomic radii. We may suppose that at the melting-point Bragg $d=$ atomic radius. Melting then may be considered to belong to the same class of phenomena as orientations—

that is, a class in which a definite temperature is characterized by a definite distance.

Thus if T° K is the melting-point, ϵ the atomic radius, x_p and x_q the Bragg d's for any two planes, $T^\circ_p K$ and $T^\circ_q K$ the temperatures at which orientations occur parallel to these planes, then we get

$$\frac{T_p}{T_q} = \frac{x_q}{x_p}$$

and

$$T_p = \frac{\epsilon T}{x_p}. \quad \text{and} \quad T_q = \frac{\epsilon T}{x_q}.$$

Hence if we know the melting-point and the atomic radius we can predict the temperatures at which orientations parallel to any plane should occur. Conversely, if it is possible to get a sufficient number of different orientations it would be possible to determine the atomic radius.

Finally, it is necessary to remember that in calculating the distances between the planes, the actual distance between the planes of any family has to be considered. For example, in the case of 100 planes of a face-centred cubic lattice the actual distance is d_{200} and not d_{100}.

A few calculations are attached of the temperatures at which orientations parallel to any plane should occur, and comparison is made with the temperature at which this orientation is observed (Table VII.).

Since each orientation can be observed over a wide range of temperature, the temperature at which it is strongest can be determined only to an accuracy of about 20° C., and the agreement is thus seen to be satisfactory. The very close agreement shown in many cases is no doubt fortuitous.

Table VII.

(†) Ag Face-centred Cubic $a = 4 \cdot 08$; Melting-point 960° C. ; Atomic Radius $1 \cdot 78$.

Planes.	d.	Temperatures of orientations.	
		Calculated.	Observed (Table III.).
$\sqrt{2}$ (111)	2·35	659° C.	650° C.
$\sqrt{4}$ (200)	2·04	801° C.	800° C.

(2) Al Face-centred Cubic $a = 4\cdot04$; Melting-point
660° C. ; Atomic Radius 1·35.

Planes.	d.	Temperatures of orientations.	
		Calculated.	Observed (Table IV.).
$\sqrt{3}$ (111)	2·33	264° C.	260° C.
$\sqrt{4}$ (200)	2·04	346° C.	350° C.
$\sqrt{8}$ (220)	1·43	602° C.	606° C.

(3) Zn Hexagonal close-packed $a_0 = 2\cdot65$, $C_0 = 5\cdot14$;
Melting-point 418° C. ; Atomic Radius 0·8.

Planes.	d.	Temperatures of orientations.	
		Calculated.	Observed (Table V.).
100	2·30	−32° C.	....
101	2·08	− 7° C.	10° C.
102	1·68	56° C.	60° C.
103, 110	1·33	143° C.	150° C.
112, 201	1·12	227° C.	200° C. ?
104	1·08	239° C.	250° C. ?
203	0·94	315° C.	300° C.
105, 114	0·905	338° C.	....

Conclusion.

We have been considering all the time the first layer
of the deposit in contact with the polished surface,
regarding this as a two-dimensional gas; we have calcu-
lated the temperatures at which the atoms in this layer
can be arranged so that a definite plane of the crystal-
lattice is parallel to the base. The base serves only as a
reasonably flat support, not deviating as far as practically
possible from a plane, and that is why its nature, if
amorphous, has no effect on the orientations. Single
crystals with natural cleavage faces, which are the best
planes obtainable, were not used, as the regular arrange-
ment of atoms might influence the arrangement in the
deposited layer. This is not likely with the amorphous
polished base.

When the first layer has a definite orientation the upper layers will tend to have the same orientation and the tendency will be the less the greater the distance between the extreme layers—that is why it is difficult to obtain orientations with thick deposits, although recrystallization is observed. The atoms in the basic layer can arrange themselves in a particular way at a definite temperature very easily, and at a temperature fairly near to this particular one with rather more difficulty. This explains why very strong orientations are seen at a definite temperature and rather weaker orientations for neighbouring temperatures. It is unlikely that any special arrangement of the atoms, when once taken place, would be destroyed unless some force is used in destroying it. That is why the orientation at the room temperature—that is, the temperature at which pictures are taken—would be the same as that at the special heat treated temperature.

It is also unlikely that the atoms in this basic layer can have two absolutely distinct arrangements, and that is why two equally distinct orientations are never seen. When two orientations are seen, and are possible, the block being maintained at an intermediate temperature, one of them is much stronger than the other. Five or six orientations, if simultaneously possible, as in the case of zinc, may be seen ; but this is almost a polycrystalline arrangement, and produces a pattern of almost complete rings with a few much stronger in the centre than is normally the case.

Finally, I wish to express my sincere thanks to Prof. Thomson for his kind help and valuable guidance, without which this work would not have been possible.

Summary.

The present work was undertaken to investigate chiefly the effect of temperature on the orientations of the small crystals in thin metallic films. The films, 10^{-4}–10^{-6} cm. thick, of silver on molybdenum, quartz, and glass, of aluminium on molybdenum, and of zinc on molybdenum have been studied over the whole range of temperatures above the room temperature. Different orientations have been observed which do not depend on the nature of the base. A theory is proposed that these thin deposits behave as a two-dimensional gas.

LXXXVIII. *A Trigonometrical Sum.* By H. S. Carslaw *and* R. J. Lyons*.

§ 1. *Introductory.*

THE sum with which this communication deals is

$$s_n = 2 \sum_1^n \frac{\sin(2r-1)x}{2r-1},$$

being the sum of n terms of the infinite series

$$2\{\sin x + \tfrac{1}{3}\sin 3x + \tfrac{1}{5}\sin 5x + \dots\}.$$

The approximation curves $y = \sigma_n(x)$, where $\sigma_n = \frac{1}{n}\sum_1^n s_r$,

are considered †. These are Fejér's Arithmetic Means, and they are found to possess the following properties. In the interval $(0, \pi)$ y is positive for every n, and each curve is symmetrical about $x = \tfrac{1}{2}\pi$. As we proceed from $x = 0$ to $x = \tfrac{1}{2}\pi$ the ordinates of the maxima and the ordinates of the minima continually increase, n being fixed. Also σ_n converges uniformly to $\tfrac{1}{2}\pi$ in (a, b), where $0 < a < b < \pi$. These properties of the curves $y = \sigma_n(x)$ give a simple proof that the Gibbs Phenomenon ‡ does not appear in the sum by arithmetic means of this trigonometrical series.

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* Communicated by the Authors.

† The properties of the approximation curves $y = s_n(x)$ for this series are given in Carslaw's 'Fourier's Series and Integrals' (3rd ed., 1930), § 115.

‡ Let $u_1(x), u_2(x), \dots$ be a sequence, and $\lim_{n \to \infty} u_n(x) = f(x)$. Further,

let x_0 be a point of ordinary discontinuity of $f(x)$.

If for large values of n the curves $y = u_n(x)$ do not tend to coincide with the line joining $\{x_0, f(x_0+0)\}$ and $\{x_0, f(x_0-0)\}$ in the neighbourhood of x_0, but project above and below the ends of this segment by an amount depending on the value of $|f(x_0+0) - f(x_0-0)|$ the sequence is said to exhibit the Gibbs Phenomenon.

Or we may say that the Gibbs Phenomenon occurs when the upper double limit

$$\overline{\lim_{x \to x_0+0, \, n \to \infty}} u_n(x) > f(x_0+0)$$

and the lower double limit

$$\lim_{x \to x_0-0, \, n \to \infty} u_n(x) < f(x_0-0),$$

taking the case when $f(x_0+0) > f(x_0-0)$.

The series

$$2 \sum_1^\infty \frac{\sin (2n-1)x}{2n-1}$$

is the Fourier's Series for $f(x)$, where $f(x) = \frac{1}{2}\pi$ when $0 < x < \pi$, and $f(x) = -\frac{1}{2}\pi$ when $-\pi < x < 0$; but in summing this Fourier's Series by Arithmetic Means we must remember that the constant term and all the even terms of the series vanish and that the term in $\sin (2n-1)x$ is not the nth term.

§ 2. Let

$$s_n = 2 \sum_1^n \frac{\sin (2r-1)x}{2r-1}.$$

Then

$$\frac{ds_n}{dx} = 2 \sum_1^n \cos (2r-1)x = \frac{\sin 2nx}{\sin x},$$

and

$$s_n = \int_0^x \frac{\sin 2nt}{\sin t}\, dt,$$

since $s_n = 0$ when $x = 0$.

Thus the Arithmetic Mean (σ_n) in the summation (C, 1) of this series is

$$\sigma_n = \frac{1}{n} \sum_1^n s_r$$

$$= \frac{1}{n} \sum_1^n \int_0^x \frac{\sin 2rt}{\sin t}\, dt$$

$$= \frac{1}{2n} \int_0^x \frac{\cos t - \cos (2n+1)t}{\sin^2 t}\, dt \quad . \quad . \quad . \quad (1)$$

$$= \frac{1}{n} \int_0^x \frac{\sin nt \sin (n+1)t}{\sin^2 t}\, dt \quad . \quad . \quad . \quad . \quad (2)$$

$$= \frac{2}{n} \sum_1^n \frac{(n-r+1) \sin (2r-1)x}{2r-1}. \quad . \quad . \quad . \quad (3)$$

The equations (1) and (2) are required in the discussion of the turning-points of the curve $y = \sigma_n(x)$; (3) is useful in obtaining numerical data for drawing the curve.

§ 3. Since $s_n(x)$ is symmetrical about $x = \frac{1}{2}\pi$ in the interval $(0, \pi)$, and is positive in this interval *, it follows that $\sigma_n(x)$ also has these properties.

* *Cf.* Carslaw, *loc. cit.* § 115, I. and II.

Further,

$$\frac{d\sigma_n}{dx} = \frac{\sin nx \sin (n+1)x}{n \sin^2 x}.$$

Therefore maximum turning-points of $y = \sigma_n(x)$ are given by $(n+1)x = r\pi$ and minimum turning-points by $nx = r\pi$, r being a positive integer. If n is odd there are $\frac{1}{2}(n+1)$ maximum turning-points in $0 \leq x \leq \frac{1}{2}\pi$, the last being at $x = \frac{1}{2}\pi$, and there are $\frac{1}{2}(n-1)$ minimum turning-points, the last being at $x = \frac{1}{2}\pi - \frac{1}{2}\frac{\pi}{n}$. If n is even there are $\frac{1}{2}n$ maximum turning-points in the same interval, the last being at $x = \frac{1}{2}\pi - \frac{1}{2}\frac{\pi}{(n+1)}$, and $\frac{1}{2}n$ minimum turning-points, the last being at $x = \frac{1}{2}\pi$.

At $x = 0$ the gradient of $y = \sigma_n(x)$ is $(n+1)$, and at $x = \pi$ it is $-(n+1)$.

§ 4. *As we proceed from $x = 0$ to $x = \frac{1}{2}\pi$ the ordinates of the minima of $y = \sigma_n(x)$ continually increase, n being fixed.*

Let the ordinates of the rth and $(r+1)$th minimum turning-points be m_r and m_{r+1}, while M_r and M_{r+1} denote the ordinates of the corresponding maxima.

Then m_r is the value of $\sigma_n(x)$ when $x = \frac{r\pi}{n}$,

and M_r is the value of $\sigma_n(x)$ when $x = \frac{r\pi}{n+1}$.

Therefore

$$m_{r+1} - m_r = (M_{r+1} - m_r) - (M_{r+1} - m_{r+1})$$

$$= \frac{1}{2n}(A - B),$$

where

$$A = \int_{\frac{r}{n}\pi}^{\frac{r+1}{n+1}\pi} \frac{\cos t - \cos (2n+1)t}{\sin^2 t} \, dt,$$

and

$$B = \int_{\frac{r+1}{n+1}\pi}^{\frac{r+1}{n}\pi} \frac{\cos (2n+1)t - \cos t}{\sin^2 t} \, dt.$$

4 B 2

In both A and B the integrand is positive in the interval of integration, since

$$\frac{d\sigma_n}{dx} = \frac{1}{2n} \frac{\cos x - \cos (2n+1)x}{\sin^2 x} \quad \text{by § 2 (1).}$$

Thus

$$A > \frac{1}{\sin^2 \dfrac{r+1}{n+1} \pi} \int_{\frac{r}{n}\pi}^{\frac{r+1}{n+1}\pi} \{\cos t - \cos (2n+1)t\}\, dt,$$

and

$$B < \frac{1}{\sin^2 \dfrac{r+1}{n+1} \pi} \int_{\frac{r+1}{n+1}\pi}^{\frac{r+1}{n}\pi} \{\cos (2n+1)t - \cos t\}\, dt$$

Therefore

$$A - B > \frac{1}{\sin^2 \dfrac{r+1}{n+1} \pi} \int_{\frac{r}{n}\pi}^{\frac{r+1}{n}\pi} \{\cos t - \cos (2n+1)t\}\, dt$$

$$> \frac{2n}{2n+1} \left(\frac{\sin \dfrac{r+1}{n} \pi - \sin \dfrac{r}{n} \pi}{\sin^2 \dfrac{r+1}{n+1} \pi} \right)$$

> 0, since, in $0 < x \leqq \frac{1}{2}\pi$, we have

$$\frac{1}{2}\pi \geqq \frac{r+1}{n} \pi > \frac{r}{n} \pi > 0.$$

It follows that $m_{r+1} > m_r$.

§ 5. *As we proceed from* $x = 0$ *to* $x = \frac{1}{2}\pi$ *the ordinates of the maxima of* $y = \sigma_n(x)$ *continually increase,* n *being fixed.*

With the same notation as in § 4,

$$M_{r+1} - M_r = (M_{r+1} - m_r) - (M_r - m_r)$$

$$= \frac{1}{2n} (C - D),$$

where
$$C = \int_{\frac{r}{n}\pi}^{\frac{r+1}{n+1}\pi} \frac{\cos t - \cos (2n+1)t}{\sin^2 t}\, dt,$$

and
$$D = \int_{\frac{r}{n+1}\pi}^{\frac{r}{n}\pi} \frac{\cos(2n+1)t - \cos t}{\sin^2 t}\, dt,$$

and the integrands in C and D are both positive in the interval of integration.

Thus
$$C > \frac{1}{\sin^2 \frac{r+1}{n+1}\pi} \int_{\frac{r}{n}\pi}^{\frac{r+1}{n+1}\pi} \{\cos t - \cos(2n+1)t\}\, dt$$

$$> \frac{1}{\sin^2 \frac{r+1}{n+1}\pi} \left\{ \left(\sin\frac{r+1}{n+1}\pi - \sin\frac{r}{n}\pi \right) \right.$$

$$\left. - \frac{1}{2n+1} \left(\sin(2n+1)\frac{r+1}{n+1}\pi - \sin(2n+1)\frac{r}{n}\pi \right) \right\}$$

$$> \frac{2}{2n+1} \left(\frac{(n+1)\sin\frac{r+1}{n+1}\pi - n\sin\frac{r}{n}\pi}{\sin^2\frac{r+1}{n+1}\pi} \right),$$

and
$$D < \frac{1}{\sin^2 \frac{r}{n+1}\pi} \int_{\frac{r}{n+1}\pi}^{\frac{r}{n}\pi} \{\cos(2n+1)t - \cos t\}\, dt$$

$$< \frac{2}{2n+1} \left(\frac{(n+1)\sin\frac{r}{n+1}\pi - n\sin\frac{r}{n}\pi}{\sin^2\frac{r\pi}{n+1}} \right).$$

Therefore
$$C - D > \frac{2n}{2n+1} \left(\frac{\left(1+\frac{1}{n}\right)\sin\frac{r+1}{n+1}\pi - \sin\frac{r}{n}\pi}{\sin^2\frac{r+1}{n+1}\pi} \right.$$

$$\left. - \frac{\left(1+\frac{1}{n}\right)\sin\frac{r}{n+1}\pi - \sin\frac{r}{n}\pi}{\sin^2\frac{r}{n+1}\pi} \right)$$

$$> \frac{2n}{2n+1} \left(\frac{\sin \frac{r+1}{n+1} \pi - \sin \frac{r}{n+1} \pi}{\sin \frac{r+1}{n+1} \pi \sin \frac{r}{n+1} \pi} \right)$$

$$\left(\frac{\sin \frac{r}{n} \pi}{\sin \frac{r}{n+1} \pi} + \frac{\sin \frac{r}{n} \pi}{\sin \frac{r+1}{n+1} \pi} - 1 - \frac{1}{n} \right),$$

on simplifying the right-hand side of the inequality.
But

$$\frac{r}{n+1} \pi < \frac{r}{n} \pi < \frac{r+1}{n+1} \pi \leqq \tfrac{1}{2}\pi.$$

Therefore

$$\frac{\sin \frac{r+1}{n+1} \pi - \sin \frac{r}{n+1} \pi}{\sin \frac{r+1}{n+1} \pi \sin \frac{r}{n+1} \pi} > 0.$$

Also, from the curve $y = \sin x / x$, we know that

$$\frac{\sin \frac{r}{n} \pi}{\frac{r}{n}} > \frac{\sin \frac{r+1}{n+1} \pi}{\frac{r+1}{n+1}},$$

and

$$\frac{\sin \frac{r}{n} \pi}{\sin \frac{r}{n+1} \pi} > 1.$$

Therefore

$$\frac{\sin \frac{r}{n} \pi}{\sin \frac{r}{n+1} \pi} + \frac{\sin \frac{r}{n} \pi}{\sin \frac{r+1}{n+1} \pi} - 1 - \frac{1}{n} > 1 + \frac{r}{r+1} \left(1 + \frac{1}{n} \right) - 1 - \frac{1}{n}$$

$$> \frac{1}{r+1} \left(r - \frac{1}{n} \right)$$

$$> 0, \text{ since } r > \frac{1}{n}.$$

Thus $C - D > 0$.

It follows that $M_{r+1} > M_r$.

§ 6. We know that the series

$$\sum_1^\infty \frac{\sin (2r-1)x}{2r-1}$$

converges uniformly to $\frac12\pi$ in (a, b), when $0 < a < b < \pi$ *.

It follows that $\sigma_n(x) \to \frac12\pi$ uniformly in such an interval †.

The results of §§ 4, 5 thus show that for all values of n greater than some definite positive integer dependent on the arbitrary positive ϵ the curves $y = \sigma_n(x)$ in $(0, \pi)$ lie within the shaded portion of fig. 1. This is bounded by the lines $x=0$, $x=\epsilon$, $x=\pi-\epsilon$, $x=\pi$, $y=0$, and $y=\frac12\pi\pm\epsilon$

Fig. 1.
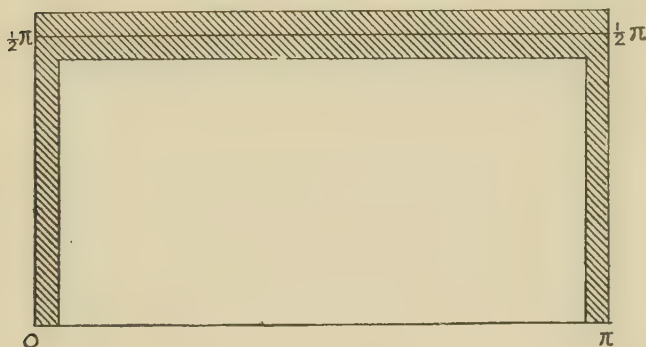
Thus the Gibbs Phenomenon does not occur in the sum by Arithmetic Means of this series.

In fig. 2 the curve $y = \sigma_6(x)$ is given, and it is interesting to compare figs. 1 and 2 with the corresponding diagrams for the ordinary sum of this series given in figs. 3 and 4.

Fig. 3 shows the existence of the Gibbs Phenomenon in the ordinary sum ; fig. 4 is the curve

$$y = \sum_1^6 \frac{\sin (2r-1)x}{2r-1}.$$

It will be seen that in the summation by Arithmetic Means the oscillations in this curve are smoothed down.

* *Cf.* Carslaw, *loc. cit.* p. 152, Ex. 4.
† *Cf.* Carslaw, *loc. cit.* § 102, Theorem I.

Fig. 2.
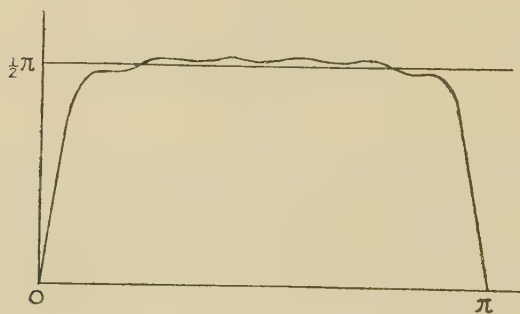
Fig. 3.
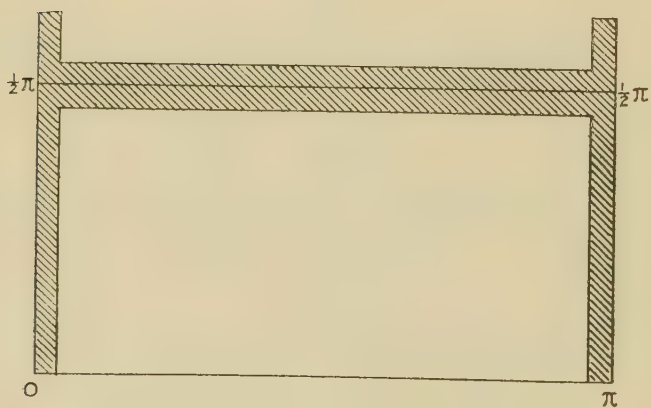
Fig. 4.
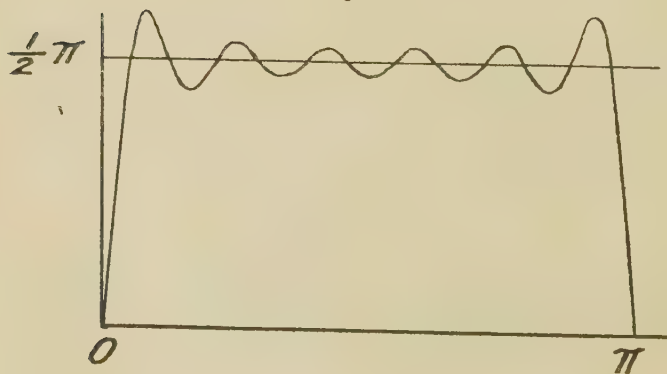
§ 7. In § 5 we have seen that the last maximum of $y = \sigma_n(x)$ in $(0, \frac{1}{2}\pi)$ has the greatest ordinate, n being fixed, and that if n is odd this maximum occurs when $x = \frac{1}{2}\pi$, while if n is even it occurs when $x = \frac{1}{2}\pi - \frac{1}{2}\dfrac{\pi}{n+1}$.

In the first case its ordinate is given by

$$y = \frac{1}{n}\int_0^{\frac{1}{2}\pi} \frac{\sin nt \sin (n+1)t}{\sin^2 t}\,dt$$

$$= \frac{1}{n}\int_0^{\frac{1}{2}\pi} \frac{\sin^2 nt}{\sin^2 t}\cos t\,dt + \frac{1}{2n}\int_0^{\frac{1}{2}\pi} \frac{\sin 2nt}{\sin t}\,dt.$$

Since

$$\lim_{n\to\infty}\int_0^{\frac{1}{2}\pi}\frac{\sin 2nt}{\sin t}\,dt = \frac{1}{2}\pi,$$

the second term vanishes when $n\to\infty$. Also

$$\frac{1}{n}\int_0^{\frac{1}{2}\pi}\frac{\sin^2 nt}{\sin^2 t}\cos t\,dt = \int_0^{\frac{1}{2}n\pi}\frac{\sin^2 t}{t^2}\left(\frac{t/n}{\sin t/n}\right)^2\cos t/n\,dt.$$

Therefore, by Tannery's theorem for integrals *,

$$\lim_{n\to\infty}\frac{1}{n}\int_0^{\frac{1}{2}\pi}\frac{\sin^2 nt}{\sin^2 t}\cos t\,dt = \int_0^\infty\frac{\sin^2 t}{t^2}\,dt.$$

Thus

$$\lim_{n\to\infty} y = \int_0^\infty\frac{\sin^2 t}{t^2}\,dt = \frac{1}{2}\pi.$$

In the second case the ordinate of the last maximum in $(0, \frac{1}{2}\pi)$ is given by

$$y = \frac{1}{n}\int_0^{\frac{1}{2}\pi - \frac{1}{2}\frac{\pi}{n+1}}\frac{\sin nt \sin (n+1)t}{\sin^2 t}\,dt$$

$$= \int_0^{\frac{1}{2}n\pi - \frac{1}{2}\frac{n\pi}{n+1}}\frac{\sin^2 t}{t^2}\left(\frac{t/n}{\sin t/n}\right)^2\cos t/n\,dt$$

$$+ \frac{1}{2n}\int_0^{\frac{1}{2}n\pi - \frac{1}{2}\frac{n\pi}{n+1}}\frac{\sin 2t}{t}\left(\frac{t/n}{\sin t/n}\right)dt$$

* *Cf.* Bromwich, 'Infinite Series' (2nd ed. 1926), p. 485.

To both these integrals we can apply Tannery's theorem, and we find, as before, that

$$\lim_{n \to \infty} y = \tfrac{1}{2}\pi.$$

A similar argument applies to the last minimum in $(0, \tfrac{1}{2}\pi)$, n being fixed, and the limit is in this case also $\tfrac{1}{2}\pi$.

The results of § 6 could be deduced from this section.

§ 8. The series

$$2 \sum_1^\infty \frac{\sin (2r-1)x}{2r-1}$$

is Fourier's series for $f(x)$, where $f(x) = \tfrac{1}{2}\pi$, when $0 < x < \pi$, and $f(x) = -\tfrac{1}{2}\pi$ when $-\pi < x < 0$; but in summing this series by arithmetic means we must remember that the term $\dfrac{2 \sin (2r-1)x}{2r-1}$ is u_{2r-1} in the Fourier's Series and that the constant term and all the even terms are zero.

Thus, if

$$s_n = \sum_0^n u_r,$$

we see that

$$s_0 = 0,$$
$$s_1 = s_2 = 2 \sin x,$$
$$s_3 = s_4 = 2 \left(\sin x + \tfrac{1}{3} \sin 3n\right).$$
$$s_{2n-1} = s_{2n} = 2 \sum_1^n \frac{\sin (2r-1)x}{2r-1}.$$

Then, if

$$\sigma_n = \frac{1}{n} \sum_0^{n-1} s_r,$$

we have

$$\sigma_{2n} = \frac{1}{2n} \sum_0^{2n-1} s_r = \frac{2 \sum_1^{n-1} s_{2r-1} + s_{2n-1}}{2n},$$

and

$$\sigma_{2n+1} = \frac{1}{2n+1} \sum_0^{2n} s_r = \frac{2}{2n+1} \sum_1^n s_{2r-1}.$$

But

$$s_{2r-1} = \int_0^x \frac{\sin 2rt}{\sin t} dt;$$

therefore

$$\sigma_{2n} = \frac{1}{2n} \int_0^x \frac{\cos t - \cos(2n-1)t}{\sin^2 t} \, dt + \frac{1}{2n} \int_0^x \frac{\sin 2nt}{\sin t} \, dt$$

$$= \frac{1}{2n} \int_0^x \frac{\cos t(1 - \cos 2nt)}{\sin^2 t} \, dt$$

$$= \frac{1}{n} \int_0^x \cos t \frac{\sin^2 nt}{\sin^2 t} \, dt.$$

Also

$$\sigma_{2n+1} = \frac{2}{2n+1} \int_0^x \frac{\sin nt \sin(n+1)t}{\sin^2 t} \, dt.$$

§ 9. In the curve

$$y = \sigma_{2n}(x) = \frac{1}{n} \int_0^x \frac{\sin^2 nt}{\sin^2 t} \cos t \, dt,$$

$$\frac{dy}{dx} = \frac{\cos x \sin^2 nx}{n \sin^2 x}.$$

Thus this curve rises continually from zero at $x=0$ to its single maximum at $x = \frac{1}{2}\pi$ in the interval $(0, \pi)$, and then descends continually to zero at $x = \pi$.

At $x = \frac{1}{2}\pi$

$$\sigma_{2n} = \frac{1}{n} \int_0^{\frac{1}{2}\pi} \frac{\sin^2 nt}{\sin^2 t} \cos t \, dt$$

$$< \frac{1}{n} \int_0^{\frac{1}{2}\pi} \frac{\sin^2 nt}{\sin^2 t} \, dt$$

$$< \frac{1}{2}\pi, \quad \text{since} \quad \int_0^{\frac{1}{2}\pi} \frac{\sin^2 nt}{\sin^2 t} \, dt = \frac{1}{2}n\pi\,[*].$$

Also

$$\lim_{n \to \infty} \sigma_{2n}(\tfrac{1}{2}\pi) = \tfrac{1}{2}\pi.$$

The properties of the curve

$$y = \sigma_{2n+1}(x) = \frac{2}{2n+1} \int_0^x \frac{\sin nt \sin(n+1)t}{\sin^2 t} \, dt$$

follow from our previous discussion.

$\sigma_{2n+1}(x)$ is positive in $(0, \pi)$ and symmetrical about $x = \frac{1}{2}\pi$; also $\sigma_{2n+1}(x) < \frac{1}{2}\pi$ in this interval [†].

* *Cf.* Carslaw, *loc. cit.* p. 256.
† *Cf.* Carslaw, *loc. cit.* p. 308.

The maximum turning-points of $y = \sigma_{2n+1}(x)$ are given by $(n+1)x = r\pi$ and the minimum turning-points by $nx = r\pi$. If n is odd there are $\frac{1}{2}(n+1)$ maxima in $(0, \frac{1}{2}\pi)$, the last being at $x = \frac{1}{2}\pi$, and there are $\frac{1}{2}(n-1)$ minima, the last being at $x = \frac{1}{2}\pi - \frac{1}{2}\dfrac{\pi}{n}$. If n is even there are $\frac{1}{2}n$ maxima in the same interval, the last being at $x = \frac{1}{2}\pi - \frac{1}{2}\dfrac{\pi}{n+1}$, and $\frac{1}{2}n$ minima, the last being at $x = \frac{1}{2}\pi$.

As we proceed from $x = 0$ to $x = \frac{1}{2}\pi$ the ordinates of the maxima and the ordinates of the minima continually increase, n being fixed *.

The last maximum is below $\frac{1}{2}\pi$, but its limit as $n \to \infty$ is $\frac{1}{2}\pi$.

Fig. 5.
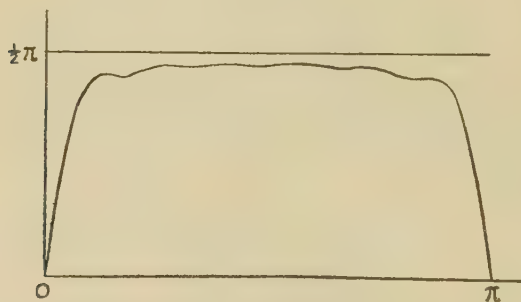
In fig. 5 the curve $y = \sigma_{2n+1}(x)$ is drawn for $n = 6$. It will be seen from the expression for $\sigma_{2n+1}(x)$ when $n = 6$ that this curve can be obtained from that of fig. 2 by reducing the ordinates in the ratio $12 : 13$; or in the general case $2n : 2n+1$.

Again, it is known that the sum by arithmetic means of this Fourier's Series converges uniformly to $\frac{1}{2}\pi$ in (a, b), where $0 < a < b < \pi$.

It follows from the properties we have obtained above for these curves that, for all values of n greater than

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* The ordinate of the single maximum of $\sigma_{2n}(x)$ in $(0, \pi)$ continually increases as n increases, so that it tends from below to its limiting value; and the ordinate of the last maximum (and minimum) of $\sigma_{2n+1}(x)$ in $(0, \frac{1}{2}\pi)$ also continually increases with n.

The proof of these results is longer, and it does not seem worth while to include it.

some definite positive integer dependent on the arbitrary positive ϵ, the curves $y = \sigma_{2n}(x)$ and $y = \sigma_{2n+1}(x)$ in $(0, \pi)$ lie within the shaded portion of fig. 6. This is bounded by the lines $x = 0$, $x = \epsilon$, $x = \pi - \epsilon$, $x = \pi$, $y = 0$, $y = \frac{1}{2}\pi - \epsilon$, and $y = \frac{1}{2}\pi$.

Thus the Gibbs Phenomenon does not occur in the sum by arithmetic means of this Fourier's Series [*].

§ 10. The behaviour of the curves $y = \sigma_n(x)$ for this series in the neighbourhood of $x = 0$, where n is any integer, odd or even, can also be described in the following way [*]:—

Fig. 6.
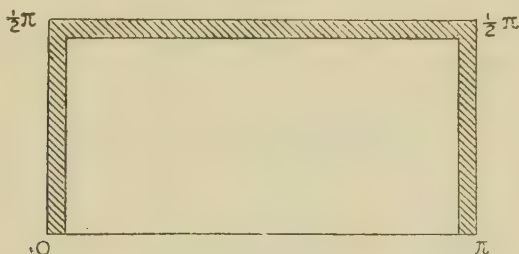
To the arbitrary positive number ϵ there corresponds a positive number η, such that, for all values of n,

$$\left| \sigma_n(x) - \int_0^{nx} \left(1 - \frac{t}{nx}\right) \frac{\sin t}{t} dt \right| < \epsilon,$$

when $0 \leqq x \leqq \eta$.

Let n be an even positive integer, say $2p$.

Then, integrating $\sigma_{2p}(x)$ by parts, we have

$$\sigma_{2p}(x) - \int_0^{2px} \left(1 - \frac{t}{2px}\right) \frac{\sin t}{t} dt$$

$$= \left\{ -\frac{1 - \cos 2px}{2p \sin x} + \int_0^x \frac{\sin 2pt}{\sin t} dt \right\}$$

$$- \left\{ \int_0^x \frac{\sin 2pt}{t} dt - \frac{1 - \cos 2px}{2px} \right\}$$

---

[*] In his paper "Über die Fouriersche Reihe," in *Math. Annalen,* Bd. lxiv. (1907), Fejér showed that the Gibbs Phenomenon does not occur when Fourier's Series is summed by Arithmetic Means. See also Carslaw, *loc. cit.* p. 308.

[*] This is a special case of Cramér's theorem ; cf. *Arkiv f. Matematik* (Stockholm), Bd. xiii. no. 20 (1918).

$$= -\frac{1-\cos 2px}{2p}\left(\frac{1}{\sin x} - \frac{1}{x}\right)$$

$$+ \int_0^x \sin 2pt\left(\frac{1}{\sin t} - \frac{1}{t}\right) dt$$

$$= -\frac{1-\cos 2px}{2p}\left(\frac{x}{\sin x}\right)\left(\frac{x}{3!} - \frac{x^3}{5!} + \dots\right)$$

$$+ \int_0^x \sin 2pt\left(\frac{t}{\sin t}\right)\left(\frac{t}{3!} - \frac{t^3}{5!} + \dots\right) dt.$$

But

$$0 \leqq \frac{x}{3!} - \frac{x^3}{5!} + \dots \leqq \frac{x}{3!}, \quad \text{when } 0 < x < \tfrac{1}{2}\pi.$$

And

$$1 \leqq \frac{x}{\sin x} \leqq \tfrac{1}{2}\pi, \qquad \text{when } 0 \leqq x \leqq \tfrac{1}{2}\pi.$$

Thus

$$\left| \sigma_{2p}(x) - \int_0^{2px}\left(1 - \frac{t}{2px}\right)\frac{\sin t}{t} dt \right| < \frac{\pi x}{12p} + \frac{\pi}{12}\int_0^x x\, dx$$

$$< \frac{\pi x}{12} + \frac{\pi x^2}{24} \quad \text{in } (0, \tfrac{1}{2}\pi) \text{ for all values of } p.$$

$$< \epsilon, \quad \text{when } 0 \leqq x \leqq \eta.$$

The case of an odd integer can be treated in the same way.

Again,

$$\int_0^{nx}\frac{\sin^2 t}{t^2} dt = -\frac{1-\cos 2nx}{2nx} + \int_0^{2nx}\frac{\sin t}{t} dt.$$

Thus we may put the above result as follows :—

To the arbitrary positive ϵ there corresponds a positive number η, such that

$$\left| \sigma_n(x) - \int_0^{\frac{1}{2}nx}\frac{\sin^2 t}{t^2} dt \right| < \epsilon, \quad \text{when } 0 \leqq x \leqq \eta,$$

for all values of n.

On the other hand, for the ordinary summation of this series we have

$$\left| s_n(x) - \int_{\cdot}^{nx} \frac{\sin t}{t}\, dt \right| < \epsilon, \quad \text{when } 0 \leqq x \geqq \eta,$$

for all values of n*.

LXXXIX. *The Association of Ionic Oscillations with the Negative Glow and Anode Glow. By* K. G. EMELÉUS, *M.A., Ph.D., and* A. H. GREGG, *Dept. of Physics, Queen's University, Belfast* †.

PERHAPS the greatest source of uncertainty in our present knowledge of discharges is ignorance of the exact part played by the regular internal fluctuations known as ionic oscillations [1]. These have, however, been studied almost exclusively with heavy currents, and tests made from time to time in this laboratory have failed to reveal their presence in the negative sections of low current glows on cold cathodes. This paper outlines a fuller study of the latter type of discharge in which we have again failed to detect oscillations from the negative glow and Faraday dark space, but have confirmed that high-frequency oscillations are associated with a localized form of anode glow [2], [3].

1. *Experimental Methods.*

Since the oscillations if present are of small amplitude the discharge-tubes must be designed to give, in general, a large oscillating volume, and to offer facility for their

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* If $n = 2p$, s_n is the approximation to the definite integral

$$\int_0^{nx} \frac{\sin t}{t}\, dt,$$

obtained by dividing the interval of integration $(0, 2px)$ into p equal parts and taking the sum of the rectangles with $2x$ as base and the ordinates at the middle points of the partial intervals as height. A similar remark applies to $\sigma_{2p}(x)$ and the integral

$$\int_0^{2px} \left(1 - \frac{t}{2px}\right) \frac{\sin t}{t}\, dt.$$

† Communicated by the Authors.

detection. Since, however, there is no reason to suppose that the state of purity of the gas used is of importance, no particular attention need be paid to the preparation of tubes in this respect, and waxed and greased joints can be used freely. Actually by the use of Apiezon products the vapour pressure of carbon compounds can be kept small. Three tubes have been used :

(i.) A 7 cm. length of pyrex 5 cm. in diameter, having for anode and cathode brass plates waxed on to the ends, and with two probes inserted 1 cm. from one end, one being a brass rod 1 cm. in diameter with its inner end flush with the wall of the main tube, and the other a 5 mm. length of 0·1 mm. diameter molybdenum wire at the centre of the main tube, the lead to it being sheathed in glass.

(ii.) A pyrex tube of the same size with anode and cathode nickel sheets 3×6 cm. arranged longitudinally 3 cm. apart. One end was closed with a brass disk, and a molybdenum wire projected into the middle of the tube as in (i.).

(iii.) A soda glass tube 20 cm. long, 1 cm. in diameter, with small nickel disk electrodes attached to sheathed iron slugs to render them mobile.

(i.) and (ii.) were run at 250–600 volts, and 10^{-5}–10^{-2} amp./cm.^{2}, in air and nitrogen-contaminated argon at 0·1–2·0 mm. pressure ; (iii.) was used in addition with a 98 per cent. helium 2 per cent. neon mixture at current densities up to 0·3 amp./cm.^{2} over the same pressure range.

For detection of oscillations there was used Lecher wires, a high-frequency LC circuit with crystal detector, a cathode ray oscillograph with a 400 volt electron beam and heterodyne wave-meters. These were coupled with the tubes either inductively or capacitatively through anode, cathode, or one of the auxiliary electrodes, or through an external auxiliary electrode. The potential of the auxiliary internal electrodes was varied from $+10$ to -50 volts relative to the space.

2. *Results for Negative Glow.*

No oscillations could be picked up from any tube in absence of an anode glow. This may show either

that the negative glow (and Faraday dark space) are inherently incapable of oscillation, or that the detecting apparatus was not sufficiently delicate. In the latter case the oscillations are certainly of small although uncertain amplitude. The former explanation might be expected from the theory of the oscillations. In a plasma a number of distinct modes can occur. The highest frequency, that of pure electronic vibrations, is approximately $10^4 n^{\frac{1}{2}}$, where n is the electron concentration. There is an intermediate frequency of the order $(m/M)^{\frac{1}{2}}$ this, where m and M are the masses of the electron and positive ion, and a limiting progressive wave with speed of the order $10^5 (Tm/M)^{\frac{1}{2}}$, where T is the electron temperature. Since in the negative glow n and T, and possibly the average value of M, vary from point to point in a line perpendicular to the cathode it has thus no definite oscillatory properties. The only chance for vibrations to occur in this line would be if one part, presumably the most heavily ionized, were to force oscillations of its own frequency in the remaining parts. This appears not to have been the case in our tubes, but the possibility cannot be excluded that under special circumstances (for example with particular geometrical arrangements of electrodes and walls) this might occur. Radial standing waves have, in fact, been detected by R. W. Revans in a cylindrical tube with the ionization, which was, however, much heavier than in our tubes, falling off rapidly longitudinally [4]. An annular form of negative glow noticed by Eméléus and Harris in argon [5] may have had a similar origin.

It is possible that absence of oscillations from the negative glow and Faraday dark space may be connected with the fact that moving striations passing away from the anode stop at the head of the positive column.

3. *Results for Anode Glow.*

These confirm the earlier observations [2], [3] that oscillations occur only when there is a highly localized anode glow. It so happens that this has invariably been not at the centre of the anode, but we suspect that it is the type of glow rather than its position which matters. An oscillating glow is smaller than the more usual form of anode spot. The oscillations were in the frequency range $10^4 - 10^6$ cycles per second, and so

probably not electronic.   We do not know how they arise. Their amplitude was too small to enable the wave-form to be taken with the oscillograph, but if they are actually of the same type as those found by Appleton and West [2] they have, from indirect evidence adduced by these authors, a strong sinusoidal fundamental.   It was noticed that they were more difficult to obtain with a tube which had been running for a time than with a tube with new electrodes, although they were not affected by deliberately contaminating the anode with grease.   This is in accord with the observation that anode spots are connected with evolution of gas from the anode under the influence of the discharge [6], but does not explain why a larger spot should not oscillate.   The only obvious difference between the large and small spots is in current density, greatest in the small spot.   This suggests that the apparent absence of oscillations from large symmetrically spaced spots is simply due to the amplitude being too small to detect.   On the other hand, it is possible that the oscillations build up through resonance between the acoustical and electrical modes of vibration of the glow, or are possibly associated with a periodicity in the emission of the gas coupling with plasma oscillations, and that the exact conditions for these can occur only with a small spot in the tubes that we have used.

Summary.

Some cold cathode glow discharges have been examined for ionic oscillations.   None have been found to originate in the negative glow and Faraday dark space, and it is pointed out that this may be connected with the fact that the proper frequencies of the ionized system vary from point to point continuously.   Earlier observations that localized anode spots oscillate have been confirmed and tentative explanations of this put forward.

References.

(1) For general references see K. K. Darrow, Bell Technical Journal, ii. p. 576 (1932).
(2) E. V. Appleton and A. G. D. West, Phil. Mag. xlv. p. 879 (1923).
(3) W. L. Brown and H. McN. Cowan, Phys. Rev. xxxviii. p. 376 (L) (1931).
(4) Private communication from Prof. O. S. Duffendack.
(5) K. G. Emeléus and N. L. Harris, Phil. Mag. iv. p. 49 (1927).
(6) C. H. Thomas and O. S. Duffendack, Phys. Rev. xxxv. p. 72 (1930).

XC. *The Effect of Heat Treatment on the Production of Frictional Electric Charges on Metals. By* P. A. Mainstone, *M.Sc., Lecturer in Physics, University College of North Wales* *.

ALTHOUGH many attempts have been made to standardize the rubbing conditions in the production of tribo-electric charges, practically no attention seems to have been devoted to the consideration of the effect of heating the surfaces, either before or at the time of measuring the charges. Shaw [1], in drawing up a tribo-electric series, found that after heating a given substance above a certain temperature, the substance changed its position in the series. This "critical temperature" ranged from 300° C. to 70° C., according to the hardness of the material, and the change from the "normal" to the "abnormal" state was generally sudden. Oxidation difficulties set an obvious upper limit to the available temperature of heating.

In a previous paper [2] the author showed that the charges produced by very light rubbing on metals in a controlled atmosphere varied in a characteristic manner with the gas-pressure. This variation is, without doubt, largely due to adsorption effects, and a similarity between the "frictional isotherms" and the adsorption isotherms of Langmuir was suggested.

Apparatus.

The method of the original measurements was modified to render possible the heating of both the insulated and earthed surfaces, the ultimate method of mounting and heating the surfaces being as shown in fig. 1. A disk of the metal, generally 32 mm. in diameter and 5 mm. in thickness, was prepared, cut across a diameter, and mounted on an insulating base with the two halves just separated. Considerable difficulty was experienced with the insulation at temperatures above about 200° C. Glass, mica, and even fused silica showed considerable leakage; a single crystal of quartz behaved much better, but a single crystal in the form of a thin plate suitable for the insulating base was not available. In the earlier experiments fused silica was used, but in the later

* Communicated by Professor E. A. Owen, M.A., B.Sc.

experiments the base was cut from a stiff sheet of mica. The split disk so mounted was fixed above a solid brass former wound with a heating coil of fine nichrome wire, the ends of the coil being fixed to insulated supports on an auxiliary pillar. The brass former was drilled to take a thermocouple inserted from below, the thermocouple just projecting into a cavity in the insulated portion of the experimental disk. The thermocouple was of nickel-nichrome, and was calibrated by means of a high-range mercury thermometer. The enclosing chamber, of brass, was 15 cm. in diameter and 18 cm. in height, and the heated surfaces were arranged to lie at its centre. The disposition of the chamber is shown in fig. 2. The entire mount for the heated surfaces was inserted or removed

Fig. 1.
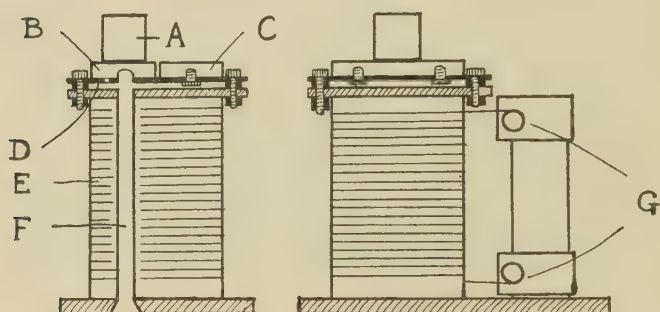
A. Quartz rubber.
B. Insulated half of metal disk.
C. Earthed   ,,   ,,   ,,   ,,
D. Insulating base.
E. Brass former with heating coil over mica layer.
F. Hole for thermocouple.
G. Insulated terminals for heating coil.

through a waxed-on window, the waxed joints of the chamber being preserved by suitable water-cooling. The rubber was a quartz cylinder 15 mm. in diameter and 15 mm. in length, with one end polished. It was moved across from one half of the split disk to the other by means of a rod passing through a taper joint, as in the previous experiments.

The temperature of heating was limited to about 350° C., owing to volatilization of zinc from the brass former, fixing screws, etc.

Effect of Heating at Low Pressure.

In the earlier experiments [2] it was suggested that at very low pressures the frictional charge on a given metal was characteristic of the metal rather than of any gas-layer adsorbed on the surface. If this assumption holds for higher temperatures, the charge should show little change. The effect of heating however, will be to bring

Fig. 2.
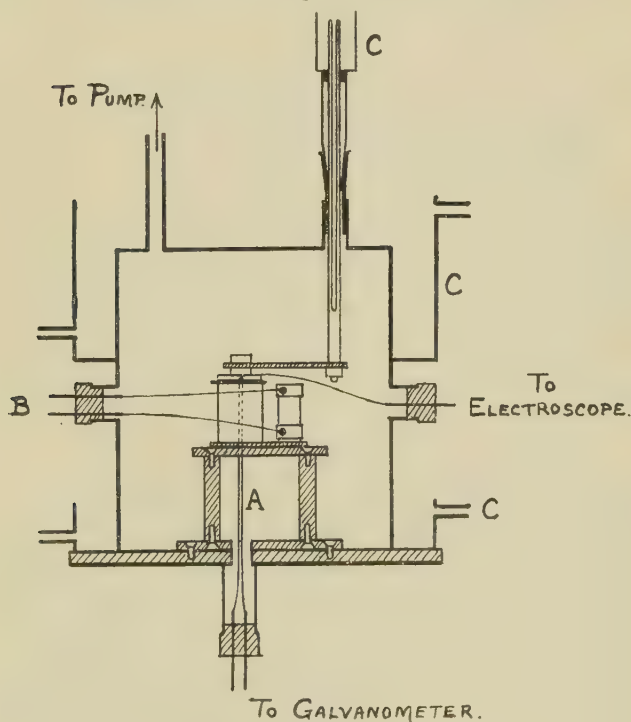
A. Thermocouple.
B. Connections for heating coil.
C. Troughs for water-cooling.

occluded gas from the interior of the metal to the surface, and some gas will almost certainly remain adsorbed, even at very low pressure, for many hours as long as heating is maintained. Further, heating may produce a permanent physical or chemical change in the surface-layer which can only be removed by repolishing.

The effect has been examined with copper, aluminium, and nickel. In each case a high vacuum was maintained by means of charcoal and liquid air, but even under these conditions considerable care was necessary in order to avoid tarnishing of the copper surfaces. This difficulty did not, as a rule, arise with either aluminium or nickel.

Preliminary experiments with each metal showed that on heating to about 300° C. the normal negative charge was considerably reduced after two or three hours'

TABLE I.

Prolonged Heating of Nickel at Low Pressure. Temperature of Heating 350° C. Initial Charge at Room-temperature —33.

Time of heating (hours)	1	2	$3\frac{1}{2}$	5	$18\frac{1}{2}$	22	27	35	52
Charge........		—18	—14	—13	—12	—4	—3	—1·5	—1·5	—1·0

After cooling to room-temperature the recovery of charge was :

Time after cooling to room-temperature (hours).	$14\frac{1}{2}$	18	21	39
Charge	—5	—8·5	—10	—16

heating, but showed a partial recovery on cooling, still at low pressure. The effect of a typical prolonged heating of nickel at 350° C. is shown in Table I. The charges throughout are given in electroscope divisions, which were approximately proportional to the potentials, and hence to the charges.

Similar results were obtained with aluminium. It is clear that the condition of the surface is permanently changed after heating, although the exact nature of this change is uncertain.

The effect of alternate heating and cooling of aluminium at low pressure is shown in Table II.

TABLE II.

Alternate Heating and Cooling of Aluminium at Low Pressure. Temperature of Heating 350° C. Initial Charge at Room-temperature −28.

After heating for 1 hour	−17
,, ,, ,, 4 hours	− 9
,, 12 hours at room-temperature	−20
,, heating for 1 hour	− 7·5
,, ,, ,, 9 hours	− 4
,, ,, 15 hours at room-temperature	−16
Air re-admitted and re-exhausted after standing for 3 hours	−19
After heating for 1 hour	− 7
,, ,, ,, 3 hours	0
,, 13 hours at room-temperature	−12·5

Effect of Heating at Atmospheric Pressure (in Nitrogen).

Experiments with both aluminium and nickel showed that the normal negative charge dropped almost to zero much more quickly than at low pressure, but that the charge again showed a partial, although slow, recovery on cooling. In some cases it appeared that this recovery only took place when the original gas was pumped off while the surfaces were still hot, and fresh gas admitted after they had cooled. This result was not, however, in general confirmed.

Frictional Isotherm at High Temperatures.

If the frictional charge at ordinary pressure is largely influenced by adsorption, the charge should certainly diminish as the temperature rises. That such a diminution takes place is already clear, but the effect of heating on the entire isotherm has not yielded altogether consistent results. The following readings for nickel, however, may be taken as typical :—

TABLE III.

Frictional Isotherm for Nickel at 300° C.

		Charge.		
State of surfaces.	Gas.	Atmos-pheric pressure.	2·5 mm.	0·25 mm.
Virgin	Air	−8·5	−5·0	−14·5
,,	Nitrogen	−7·0	− 4·0	−15·0
Heated to 300° C.	Nitrogen	−2·0	−1·0	− 5·0

The reduction of charge at ordinary pressure is as might be expected, but the large reduction at low pressure, when the amount of adsorbed gas is very small, must

TABLE IV.

Isotherms for Aluminium at Room-temperature.

Treatment immediately preceding	Gas.	Charge.		
		Atmospheric pressure.	2·5 mm.	0·25 mm.
1. Virgin surfaces (no heating)	Air	−15	− 9·5	−20
2. De-gassed 1 hour at 300° C. *in vacuo.* Air admitted when cold .	Air	−16	−11·5	−14
3. Further de-gassed 1½ hours at 300° C. Surfaces re-polished	Air	−17·5	−14	−21
4. De-gassed 1 hour at 300° C.	Air	−16	−13	−10
5. Further de-gassed 1 hour at 300° C.	Air	−14	−12	−10
6. Heated 1½ hours at 300° C. in nitrogen ..	Nitrogen	+10	+ 8	+ 9
7. De-gassed 1 hour at 300° C. Air admitted.	Air	− 0·5	+ 1·5	+ 2·5
8. Further de-gassed 1 hour at 300° C.......	Air	− 5·5	− 4·5	− 4
9. Heated 2 hours at 300° C. in nitrogen ..	Nitrogen	+ 9	+ 7·5	+11
10. De-gassed 2 hours at 300° C. Heated 2 hours at 300° C. in air. Surfaces re-polished .	Air	−17	− 11·5	7
11. De-gassed 2 hours at 300° C. Hydrogen admitted when cold. Heated 1½ hours at 300° C.	Hydrogen	+ 5·5	+23*	+50†
12. De-gassed 2 hours at 300° C. Air admitted.	Air	+14·5	+ 6·5	+27·5
13. Surfaces removed and etched.............	Air	−16	−10	−20·5

* Pressure 0·6 mm.   † Pressure 0·1 mm.

probably again be explained by changes in the surface layer of the metal. No attempt was made to obtain the isotherm at high temperatures in air, owing to oxidation risks.

Isotherm at Room-temperature after Various Treatments.

The effects of de-gassing and of sorption at temperatures of about 300° C. were carefully examined in the case of aluminium, the charges being measured after the surfaces had cooled. The charge per single rub does not reach a steady value until after a large number of rubs, and in

TABLE V.

Isotherms for Nickel at Room-temperature.

Treatment immediately preceding	Gas.	Charge.		
		Atmo-spheric. pressure.	2·5 mm.	0·25 mm.
1. Virgin surfaces	Nitrogen	− 7·0	− 4·0	−15·0
2. Isotherm at 300° C. (see Table III.).				
3. De-gassed for 1½ hours at 300° C.	Air	−11·0	−12·5	−36·0
4. Further de-gassed for 2 hours	Air	− 8·5	− 3·0	−26·0
5. Further de-gassed for 1½ hours. Hydrogen admitted and heated for ½ hour at 300° C.	Hydrogen	? 0	? 0*	?− 8·0†
6. Fresh hydrogen admitted and heated for 1½ hours at 300° C....	Hydrogen	− 0·5	− 4·0	−12·0
7. Surfaces re-polished ...	Air	−15·0	− 8·0	−23·0
8. De-gassed for 1½ hours, then heated for 2 hours at 300° C. in nitrogen.	Nitrogen	− 3·0	− 3·0	− 6·5

* Pressure 0·75 mm.   † Pressure 0·15 mm.

some of the readings the steady condition was not actually reached. This, however, does not affect the general significance of these readings.

A number of conclusions may be drawn from these readings :—

(1) Any heat-treatment entirely changes the isotherm obtained with virgin surfaces. The first de-gassing flattens out the trough of the normal isotherm.

(2) Re-polishing or etching very largely restores the original conditions, while heating in air without re-polishing does not.

(3) Heating in nitrogen, and particularly in hydrogen, may produce considerable positive charges. These may revert to negative, although not to the original values, after further de-gassing and heating in air.

A similar series of readings for nickel is shown in Table V.

Although considerable changes in the original conditions are found, there is no actual reversal of sign of the charge, as in the case of aluminium. If this reversal is due to occlusion, then it is probable that, at any rate in the case of hydrogen, the amount of gas occluded at 300° C. is very small. The possibility of the formation of hydrides or nitrides in the surface-layers must not, however, be overlooked.

Palladium.

The case of palladium in relation to the occlusion of hydrogen is so important that a considerable amount of time was spent in examining the effects of occlusion at different temperatures. A virgin surface in air gave the normal pressure variation, with negative charge throughout. After de-gassing the surfaces, hydrogen was admitted to atmospheric pressure, and after very brief heating to 250° C. a small positive charge was observed on cooling. Further heating at 300° C. gave a small positive charge, but on reducing the pressure to the order of 0·1 mm. the positive charge became much larger, and persisted even after the surfaces were partially de-gassed. The large increase in charge on reducing the pressure has been established as a definite effect when the surfaces are freshly polished, but it appears to occur also when, due to the occlusion of hydrogen, the charge has changed its sign.

As in all other cases examined, no amount of de-gassing or heating in air served to restore the surfaces to their original state, and it was necessary to remove and re-polish them before each new treatment.

The variation of the amount of occlusion and adsorption with temperature has been very exhaustively studied, and it appears certain that the amount of

occlusion increases, while the adsorption decreases, with rising temperature. It is well established, however, that in the case of some metals discontinuities exist in the adsorption isobars, and it may be that the occlusion effect is also discontinuous. There is, further, the important question as to whether the occluded hydrogen is atomic or molecular, and whether these states might be determined by the temperature. Accordingly a careful examination was undertaken of the frictional charge after occlusion at various temperatures. After each set of observations at a given temperature the surfaces were de-gassed, generally at about 250° C., re-polished, and tested for the normal negative charge before re-heating was commenced. The pressure of the hydrogen, which was generated by electrolysis, and dried before admission to the chamber, was generally between $\frac{1}{2}$ and $\frac{3}{4}$ atmosphere. The following results were obtained in this manner ; they are recorded in the sequence in which they were obtained :—

TABLE VI.

Palladium in Hydrogen.

No. of reading.	Temperature of occlusion.	Charge.	
1....	150 ° C.	After 3 hours' heating at initial pressure	— 4·0
2....	,,	After further 2 hours' heating	0
3....	,,	At reduced pressure (0·1 mm.) following no. 2	+ 7·0
4....	125° C.	After 3 hours' heating at initial pressure.	— 2·0
5....	,,	After further 2 hours' heating	0
6....	,,	At reduced pressure following no. 5 ..	0
7....	100° C.	After 3 hours' heating at initial pressure.	— 5·0
8....	,,	After further 2½ hours' heating	— 6·0
9....	,,	At reduced pressure following no. 8 ..	—16·0
10....	175° C.	After 2 hours' heating at initial pressure.	0
11....	,,	At reduced pressure following no. 10 .	+ 2·0
12....	200° C.	After 2 hours' heating at initial pressure.	— 4·0
13....	,,	After further 2 hours' heating	— 6·0
14....	,,	At reduced pressure following no. 13..	— 5·0

Although a positive charge appeared in the third reading at 150° C., this effect was not confirmed in later readings. The following series was obtained with the surfaces de-gassed *before and after* each re-polishing :—

TABLE VII.

Palladium in Hydrogen.

No. of reading.	Temperature of occlusion.	Charge.	
1....	275° C.	After 1 hour's heating at initial pressure.	$+$ 2·0
2....	,,	At reduced pressure following no. 1 ...	$\div$17·0
3....	250° C.	After ½ hour's heating at initial pressure.	$+$*
4....	225° C.	After 1 hour's heating at initial pressure.	$-$ 1·0
5....	,,	After further 1 hour's heating	$-$ 1·5
6....	,,	At reduced pressure following no. 5 ...	$-$ 1·5
7....	200° C.	After 2 hours' heating at initial pressure.	$-$ 1·0
8....	,,	At reduced pressure following no. 7 ..	$-$ 2·0

* Value not recorded.

It is clear that in this case a definite change occurs at about 250° C., and it is now considered that the appearance of positive charge at 150° C. is uncertain.

If the occlusion of hydrogen is deep-seated, and is responsible for the appearance of positive charge at 250° C., it might be expected that re-polishing without de-gassing would fail to destroy this positive charge. This, however, was not found to be the case. The surfaces were re-polished after 6 hours' occlusion at 250° C., upon which the normal negative charge appeared. It is, of course, possible that, even assuming the existence of deep-seated occlusion, the process of polishing restores the surface more or less to its original state.

Discussion.

The normal negative charge which appears on most metals when lightly rubbed with glass at ordinary temperature, and in an atmosphere of gas at ordinary

pressure, has been suggested by the author as due to rubbing on the adsorbed gas-layer rather than on the metal itself. Transfer of electrons from the glass to the gas would explain the effect, or, alternatively, the adsorbed gas may be ionized, the action of rubbing being to remove positive ions from the metal. The large negative charges appearing at very low pressures have been tentatively explained as due to rubbing on the metal itself.

Before discussing the results of the present experiments in the light of this simple theory, it may be well to state briefly the views commonly held as to the origin of frictional charges. Most important of these is that the charges appearing when the two surfaces are separated are largely due to a true static contact effect as distinct from rubbing. This, together with other views, has been recently discussed by Shaw and Leavey [3] in connexion with experiments on the rubbing of silica on a number of pure metals. It is represented as due in part to electron sharing and in part to interchange of ions, as in the case of a metal dipping into an electrolyte. Shaw and Leavey conclude that in the case of a number of metals this effect is, in fact, a major one.

The other factors are classified broadly by Shaw and Leavey as (1) surface strain and possible heating during rubbing; (2) adsorbed films and other impurities; (3) true rubbing effect. In the present experiments, where the rubbing action is so light, the first of these need not be further considered.

Returning now to the simple theory of adsorption of neutral atoms or molecules, as mentioned above, the first effect of heating at ordinary pressure will in general be to diminish the surface-density of the adsorbed gas-layer, and this, on the foregoing hypothesis, would lead to a reduction in the negative charge. In addition, however, gas occluded within the metal will be liberated, and some of this may conceivably remain adsorbed on the surface for a considerable time. The surface itself may also be changed by heating either in molecular or in grain structure. In a previous paper, however, the author has shown [4] that the charges developed on the surfaces of single crystals of aluminium and copper do not sensibly differ from those on corresponding surfaces of the metals in the polycrystalline state.

On heating at very low pressure, the original negative charge is found to diminish slowly, but to recover in part on cooling. This might conceivably be explained by the gradual evolution of gas from the metal, the gas failing to evaporate immediately (using the term "evaporate" in the sense familiar to workers on adsorption) as long as heating is maintained. On cooling, however, the evaporation proceeds more rapidly, and the surface returns in part to its original state. It must be admitted that, while true adsorption and evaporation are rapid processes, the partial recovery of the surfaces in the present case lasted for periods of several hours.

The positive charges observed in the case of occlusion of hydrogen and nitrogen by aluminium and of hydrogen by palladium clearly require other explanation. The following suggestions are put forward tentatively :—

(a) *At Low Pressures.*—An easy detachment of electrons from the metal surface provides the simplest explanation. The possibility of such a condition is supported by at least two independent lines of research. Thus Kruger and Ehmer [5] have found that the photo-electric emission from palladium-silver alloys varies with the amount of hydrogen occluded. A similar measurement with palladium alone does not appear to have been made. Also Cochn and Specht [6], in experiments on the electrical conductivity of a palladium wire containing occluded hydrogen, consider that the results indicate the presence of protons within the wire. In both researches it is held that the occluded hydrogen exists in the atomic state. If the photoelectric emission from the surfaces could be measured in the present case a direct relation between the emission and the positive frictional charge might be found.

(b), *At Ordinary Pressures.*—The simplest assumption is that the adsorbed gas-molecules are ionized, negative ions being removed by the action of rubbing. This assumption is, of course, quite arbitrary in the absence of other confirmation. The various types of adsorption on hot surfaces have been discussed by Finch and Stimson [7] in a series of papers in which they find that metallic surfaces when heated to temperatures from 500° C. to 800° C. may acquire potentials, sometimes positive, sometimes negative, of the order of 1 volt.

Thus, to quote an example, gold when heated to 510° C. acquired a negative potential *in vacuo* or in hydrogen, but a positive potential in oxygen. The adsorbed gases must be ionized, positive ions leaving the surface in the case of hydrogen, and negative in the case of oxygen. The *in vacuo* charge is considered due to ionization or " activation " of the vapour of the metal itself.

Some theoretical aspects of adsorption have been recently discussed by Lennard-Jones [8], and the following points of interest may be cited :—

1. Adsorption of atoms of a diatomic gas will take place when the potential energy of a single gaseous atom relative to the metal surface is at least equal to the dissociation energy of the gas-molecule.

2. In some cases an adsorbed gas-atom may give up an electron to the metal, when the energy of the electrons in the metal is lower than that of the electron in the atom.

3. At high temperatures the cohesion between an adsorbed gas-atom and a metallic atom may be strong enough to cause a permanent combination resulting in a tearing away of the metal atom when desorption takes place. It is not clear, however, whether such a disruption would leave the metal charged.

The state of the quartz rubbing surface in these experiments may quite possibly prove a factor in the explanation of the results. It is generally recognized that the amount of gas adsorbed on glass at ordinary temperatures is very small, and while it is known to be very difficult to drive off all occluded gas by heating, it is not likely that large quantities of gas are occluded or driven off during these experiments.

To return, finally, to the contact theory, it is clearly difficult to make any attempt at fitting it to the present case. While the effect of temperature on electron emission from a metal is known, its effect on electron interchange between a metal and glass or quartz can hardly be predicted. With regard to the interchange of ions, the potential of a metal in an electrolyte is given by Nernst's theory of solution pressure as proportional to T log P/p, where T is absolute temperature, P electrolytic solution pressure of the metal, and p the osmotic pressure of the ions in solution. In the present case

P must presumably be taken to represent vaporizing tendency and p vapour-pressure. The potential difference between metal and quartz will be proportional to

$$\mathrm{T}\left[\frac{1}{v_1}\log \mathrm{P}_1/p_1 \sim \frac{1}{v_2}\log \mathrm{P}_2/p_2\right],$$

where P_1 and p_1 relate to the metal, and P_2 and p_2 to the quartz ; v_1 and v_2 are the respective valencies of the metal and of ions leaving the quartz. While each P and p doubtless increases with temperature, it is clearly impossible to predict the variation of the entire expression.

Summary.

1 Prolonged heating of aluminium and nickel at very low pressures is shown to produce a considerable lowering of the normal negative frictional charge, with a partial slow recovery after the metal surface has been re-cooled. A similar effect is found on heating these metals in nitrogen at atmospheric pressure.

2. Widely varying results may be obtained after de-gassing the metal and re-heating it at about 300° C. in hydrogen or nitrogen. Re-polishing or etching, however, very largely restores the surface to its original state.

3. The frictional charge on polished palladium changes sign from negative to positive when the metal is de-gassed and heated in hydrogen at about 250° C.

4. The results are discussed in the light of experimental and theoretical work on adsorption, as well as in relation to the contact theory of tribo-eletricity.

It is a pleasure to record my indebtedness to Professor E. A. Owen for his continued help and advice.

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Bangor, July 1933.

XCI. *The Wave-Statistical Theory of Radioactive Disintegration.* *By* K. C KAR *and* A. GANGULI [*].

Introductory.

AFTER the well-known works of Gamow [†] and Gourney and Condon [‡] several others [§] have attempted to study the phenomena of radioactive disintegration from the standpoint of wave-mechanics, and to explain the well-known Geiger-Nuttal relation connecting the disintegration constant and the velocity of the emitted α-particle. In all these works it has been admitted that the phenomena are due to some sort of damping. But as the exact physical nature of the wave equation of Schrödinger is not known in wave-mechanics the previous investigators on the subject have not been able to make full use of the idea of damping. Accordingly their methods of treatment have been rather roundabout and unnecessarily complicated.

We may remark at the outset that the present wave-statistical [||] treatment is based on the Rutherford model, according to which a nucleus consists of a hard core surrounded by a spherical shell filled with partially polarized circulating neutral helium atoms. The positive charge of the hard core, which is packed with α- and β-particles, is therefore the positive charge of the nucleus.

It has already been pointed out by the senior author [¶] of this paper that the phase space corresponding to the nucleus, especially the hard core, is very dense, and so the phase density there gradually decreases, resulting in spontaneous emission of radioactive particles. Thus the phase space for the core becomes analogous to a compressible and also viscous fluid. Therefore the funda-

mental equations of wave-statistics based on the assumption of compressibility, namely,

$$\frac{d\mathrm{D}}{dt} + \overset{3}{\underset{1}{\Sigma}} \left(\frac{\partial \mathrm{D}}{\partial q_s} \cdot \frac{\partial \mathrm{E}}{\partial p_s} - \frac{\partial \mathrm{D}}{\partial p_s} \cdot \frac{\partial \mathrm{E}}{\partial q_s} \right) = \pm 2\pi i \nu \mathrm{D}, \quad . \quad (1)$$

on solving,

$$\mathrm{D} = \frac{\mathrm{N}}{\Phi} \chi_1 \chi_2 e^{\frac{\psi_s + \psi - \mathrm{E}}{\mathrm{KT}}} \cdot e^{\pm 2\pi i \nu t} \quad . \quad . \quad . \quad (2)$$

and

$$\frac{d^2 \mathrm{D}}{dt^2} = v_1{}^2 \varDelta \mathrm{D} \quad \text{for } q\text{-space} \quad . \quad . \quad (3)$$

$$\frac{d^2 \mathrm{D}}{dt^2} = v_2{}^2 \varDelta \mathrm{D} \quad \text{for } p\text{-space} \quad . \quad . \quad (4)$$

should now be modified for the core, and we have

$$\frac{d\mathrm{D}}{dt} + \overset{3}{\underset{1}{\Sigma}} \left(\frac{\partial \mathrm{D}}{\partial q_s} \cdot \frac{\partial \mathrm{E}}{\partial p_s} - \frac{\partial \mathrm{D}}{\partial p_s} \cdot \frac{\partial \mathrm{E}}{\partial q_s} \right) = (\pm 2\pi i \nu - b)\mathrm{D}, \quad (1a)$$

$$\mathrm{D} = \frac{\mathrm{N}}{\Phi} \chi_1 \chi_2 e^{\frac{\psi_s + \psi - \mathrm{E}}{\mathrm{KT}}} e^{\pm 2\pi i \nu t} e^{-bt}, \quad . \quad . \quad (2a)$$

$$\frac{d^2 \mathrm{D}}{dt^2} + 2b_1 \frac{d\mathrm{D}}{dt} = v_1{}^2 . \varDelta \mathrm{D} \text{ for } q\text{-space}, \quad (3a)$$

$$\frac{d^2 \mathrm{D}}{dt^2} + 2b_2 \frac{d\mathrm{D}}{dt} = v_2{}^2 . \varDelta \mathrm{D} \text{ for } p\text{-space}, \quad (4a)$$

where N is the total number of phase points, D the phase density, Φ the phase volume, b the damping coefficient, ν the frequency of the wave, v_1, v_2 velocities of the waves in the q, p spaces, and χ_1, χ_2 functions of q's and p's respectively.

Section A.

Let us first consider the modified χ_1 waves in q space. As in this case the frequency $\nu = \dfrac{2\mathrm{E}}{h}$, we have, from $(2a)$ and $(3a)$,

$$v_1{}^2 \varDelta \chi_1 + \frac{16\pi^2}{h^2} (\mathrm{E} \pm i b_1 h / 4\pi)^2 \chi_1 \mp \frac{8\pi i b_1}{h} (\mathrm{E} \pm i b_1 h / 4\pi) \chi_1 = 0,$$

$$. \quad . \quad . \quad (5)$$

which, on simplifying, becomes

$$v_1{}^2 \Delta \chi_1 + \frac{16\pi^2}{h^2}\Big(\mathrm{E} \pm \frac{ib_1 h}{4\pi}\Big)\Big(\mathrm{E} \mp \frac{ib_1 h}{4\pi}\Big)\chi_1 = 0, \quad . \quad (6)$$

or

$$v_1{}^2 \Delta \chi_1 + \frac{16\pi^2}{h^2}\Big(\mathrm{E}^2 + \frac{b_1{}^2 h^2}{16\pi^2}\Big)\chi_1 = 0, \quad . \quad (6a)$$

or, since $v_1{}^2 = \dfrac{2(\mathrm{E}-\mathrm{V})}{m}$, we have *

$$\Delta \chi_1 + \frac{8\pi^2 m}{h^2}(\mathrm{E}-\mathrm{V})\Big(1 + \frac{b_1{}^2 h^2}{16\pi^2 \mathrm{E}^2}\Big)\chi_1 = 0. \quad . \quad (7)$$

Remembering that

$$v_2{}^2 = \frac{\mathrm{E}^2 \alpha^2}{2m(\mathrm{E}-\mathrm{V})} \quad \text{and} \quad \nu = \frac{\mathrm{E}}{h},$$

we have, from $(2a)$ and $(4a)$, for χ_2 wave equation corresponding to (7), in the same way as above,

$$\Delta \chi_2 + \frac{8\pi^2 m}{\alpha^2 h^2}(\mathrm{E}-\mathrm{V})\Big(1 + \frac{b_2{}^2 h^2}{4\pi^2 \mathrm{E}^2}\Big)\chi_2 = 0, \quad . \quad (8)$$

and hence

$$\Delta \chi_3 + \frac{8\pi^2 m}{h^2}(\mathrm{E}-\mathrm{V})\Big(1 + \frac{b_2{}^2 h^2}{4\pi^2 \mathrm{E}^2}\Big)\chi_3 = 0. \quad . \quad (9)$$

As, however, the undamped χ_1 and χ_3 equations are identical, it is expected that the damped equations should also be the same. This is only possible if $b_1 = 2b_2$, giving an important relation between the two damping coefficients. Thus, as the χ_1, χ_2, and χ_3 equations are identical, except, of course, the constant α in the case of the χ_2 wave, it would be sufficient for our purpose to use the χ_1 equations in the following treatment.

Inside the hard core the potential energy is zero, but there is damping resulting in spontaneous emission of α-particles. We suppose, as a first approximation, that just outside the core the Coulomb potential is negligible; but the potential energy U_0 is constant, being the energy required to overcome the boundary potential, and a constant depending on the structure of the shell outside.

* Because for Bohr orbit $-\mathrm{E} = \mathrm{E}-\mathrm{V}$, the sign of V will be negative. For linear oscillator it will be negative for reasons explained before.— K. C. K.

Thus the χ_1 equations inside and outside the hard core are

$$\Delta\chi_1 + \frac{8\pi^2 m\mathrm{E}}{h^2}\left(1 + \frac{b_1{}^2 h^2}{16\pi^2\mathrm{E}^2}\right)\chi_1 = 0 \quad \text{(inside)}, \quad (10)$$

$$\Delta\chi_1 + \frac{8\pi^2 m}{h^2}(\mathrm{E}+\mathrm{U}_0)\chi_1 = 0. \quad \ldots \quad (11)$$

The corresponding R equations are

$$\frac{d^2\mathrm{R}}{dr^2} + \frac{2}{r}\frac{d\mathrm{R}}{dr} + \frac{8\pi^2 m}{h^2}\mathrm{E}\left(1 + \frac{b_1{}^2 h^2}{16\pi^2\mathrm{E}^2}\right)\mathrm{R} = 0, \quad (12)$$

$$\frac{d^2\mathrm{R}'}{dr^2} + \frac{2}{r}\frac{d\mathrm{R}'}{dr} + \frac{8\pi^2 m}{h^2}(\mathrm{E}+\mathrm{U}_0)\mathrm{R}' = 0. \quad (13)$$

The solutions of (12) and (13) are

$$\mathrm{R} = \text{const.}\frac{\sin\alpha r}{r}, \qquad \alpha^2 = \frac{8\pi^2 m\mathrm{E}}{h^2}\left(1 + \frac{b_1{}^2 h^2}{16\pi^2\mathrm{E}^2}\right), \quad (14)$$

$$\mathrm{R}' = \text{const.}\frac{\sin\alpha' r}{r}, \quad \alpha'^2 = \frac{8\pi^2 m}{h^2}(\mathrm{E}+\mathrm{U}_0). \quad \ldots \quad (15)$$

From conditions of continuity * we get

$$\left[\frac{\partial\log\mathrm{R}}{\partial r}\right]_{r=r_0} = \left[\frac{\partial\log\mathrm{R}'}{\partial r}\right]_{r=r_0},$$

or

$$\alpha\cot\alpha r_0 - \frac{1}{r_0} = \alpha'\cot\alpha' r_0 - \frac{1}{r_0}, \quad \ldots \quad (16)$$

which gives

$$\alpha = \alpha'. \quad \ldots \quad \ldots \quad (17)$$

Hence, from the values of α and α' given in (14) and (15) we get for damping coefficient

$$b_1 = \frac{4\pi}{h}\sqrt{\mathrm{U}_0\mathrm{E}}. \quad \ldots \quad \ldots \quad (18)$$

It is evident that the above relation may be obtained by comparing equations (12) and (13) at the boundary

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* Kudar, *l. c.* Strictly speaking we ought to take RR_2, $\mathrm{R}'\mathrm{R}_2'$ instead of simply R and R', where R_2, R_2' are the R functions for the χ_2 waves, but as $\mathrm{R}=\mathrm{R}_2$ and $\mathrm{R}'=\mathrm{R}_2'$, it makes no difference.

$r=r_0$. It may be remarked that if we put $b_1=4\pi\lambda_1$, then λ_1 will be the linear damping coefficient, and we have

$$\lambda_1=\frac{1}{h}\sqrt{U_0 E}. \quad . \quad . \quad . \quad . \quad (19)$$

From (18) and (19) it follows that the circular or linear damping coefficient is proportional to the velocity of the α-particles.

Section B.

In this section we shall discuss the same problem as above by taking into account the Coulomb potential outside the core.

The R′ equation (13) must now be modified, and we have

$$\frac{d^2 R'}{dr^2}+\frac{2}{r}\frac{dR'}{dr}+\frac{8\pi^2 m}{h^2}(E+U_0-V(r))R'=0, \quad (20)$$

where $V(r)=\dfrac{2eZ^*e}{r}$, Z^*e being the effective charge of the nucleus. On transforming (20) by putting $R'=\dfrac{R''}{r}$, we get

$$\frac{d^2 R''}{dr^2}+\frac{8\pi^2 m}{h^2}(E+U_0-V(r))R''=0. \quad . \quad . \quad (21)$$

On putting $\rho=\alpha_0 r$, α_0 being $\dfrac{4\pi\sqrt{2m(E+U_0)}}{h}$, eq. (21) is easily transformed into

$$\frac{d^2 R''}{d\rho^2}+\left(\frac{1}{4}-\frac{K}{\rho}\right)R''=0, \quad . \quad . \quad . \quad (22)$$

where

$$K=\frac{\alpha_0 Z^*.e^2}{2(E+U_0)}=\frac{4\pi Z^* e^2}{h\sqrt{2(E+U_0)/m}}=\frac{4\pi Z^* e^2}{h\sqrt{2E/m}}\left(1-\frac{1}{2}\frac{U_0}{E}\right).$$
$$. \quad . \quad . \quad (23)$$

The asymptotic solution of (22) is *

$$R''=\text{const.}\sqrt{\cot u}\,e^{K(2u-\sin 2u)}, \quad . \quad . \quad . \quad (24)$$

where

$$\cos^2 u=\rho/4K. \quad . \quad . \quad . \quad . \quad (24a)$$

* Gamow and Hautermans, *l. c.*

The solution for inside the core remains unchanged; so that, corresponding to (16), we have

$$\alpha \cot \alpha r_0 - \frac{1}{r_0} = \left\{ \frac{d}{dr} \log R' \right\}_{r=r_0}, \quad \text{and from (24)} \\ = \left\{ \frac{d}{dr} \log \frac{\sqrt{\cot u}\, e^{K(2u - \sin 2v)}}{r} \right\}_{r=r_0}. \tag{25}$$

From (14) we have approximately

$$\alpha r_0 = \sqrt{\frac{8\pi^2 m E}{h^2}} \cdot r_0 + \sqrt{\frac{8\pi^2 m E}{h^2}} \cdot \frac{b_1^2 h^2}{32\pi^2 E^2} r_0 = A + B, \tag{26}$$

so that the left-hand side of (25) becomes

$$\alpha \cot (A + B) - \frac{1}{r_0} = \alpha \{ \cot A - B(1 + \cot^2 K) \} - \frac{1}{r_0}$$

$$= \alpha \cot A - \frac{1}{r_0}, \quad \text{B being small,} \tag{27}$$

$$= \frac{\alpha}{A} - \frac{1}{r_0}, \quad \text{approximately,} \tag{27a}$$

and, substituting for α and A from (14) and (26),

$$= \frac{1}{r_0} \left(1 + \frac{b_1^2 h^2}{32\pi^2 E^2} \right) - \frac{1}{r_0}. \tag{28}$$

Again, after differentiating and transforming, the right-hand side of (25) becomes

$$-\frac{1}{r_0} + \frac{\alpha_0}{16 K \sin^2 u_0 \cos^2 u_0} - \frac{\alpha_0}{2} \tan u_0, \\ \text{where} \quad \cos^2 u_0 = \rho_0 / 4K, \quad \rho_0 = \alpha_0 r_0. \tag{29}$$

Equating (28) and (29), we get

$$\frac{1}{r_0} \left(1 + \frac{b_1^2 h^2}{32\pi^2 E^2} \right) = \frac{1}{4 r_0} \cdot \frac{4K}{4K - \alpha_0 r_0} - \frac{\alpha_0}{2} \cdot \sqrt{\frac{4K - \alpha_0 r_0}{\alpha_0 r_0}}. \tag{30}$$

As $\alpha_0 r_0 << K$, eq. (30) reduces to

$$1 + \frac{b_1^2 h^2}{32\pi^2 E^2} = \frac{1}{4} - \sqrt{\alpha_0 r_0 K}, \tag{31}$$

and substituting for K from (23), and putting $v = \sqrt{\dfrac{2E}{m}}$,

$$= \frac{1}{4} - \sqrt{\alpha_0 r_0 \cdot \frac{4\pi Z^* e^2}{hv}} \left(1 - \frac{1}{2} \frac{U_0}{E} \right)^{\frac{1}{2}}$$

$$= \frac{1}{4} - \sqrt{\frac{4\pi\alpha_0 r_0 Z^* e^2}{hv}} + \frac{1}{4} \sqrt{\frac{4\pi\alpha_0 r_0 Z^* e^2}{hv}} \cdot \frac{U_0}{E}. \quad (32)$$

On equating terms of the same order *, we get from (32)

$$1 = \frac{1}{4} - \sqrt{4\pi\alpha_0 r_0 Z^* e^2 / hv}, \quad . \quad . \quad (33a)$$

and

$$\frac{b_1^2 h^2}{32\pi^2 E^2} = \frac{1}{4} \frac{U_0}{E} \sqrt{\frac{4\pi\alpha_0 r_0 Z^* e^2}{hv}}. \quad . \quad . \quad (33b)$$

As $b_1 = 4\pi\lambda_1$, (33b) gives

$$\lambda_1 = \frac{1}{h} \sqrt[4]{\frac{\pi\alpha_0 r_0 Z^* e^2}{hv}} \cdot \sqrt{U_0 E}. \quad . \quad . \quad (34)$$

From (33a) we have

$$r_0 = \frac{9}{64\pi} \frac{hv}{\alpha_0 Z^* e^2}. \quad . \quad . \quad . \quad (35)$$

Now

$$e = 4 \cdot 77 \times 10^{-10}, \quad v = 1 \cdot 6 \times 10^9 \text{ (rad. em.) cm./sec.},$$
$$h = 6 \cdot 5 \times 10^{-27}, \quad Z^* = Z - 2 = 84.$$

Substituting these values, we get from (35)

$$r_0 \sim 1 \cdot 20 \times 10^{-15}.$$

With the above value of r_0 we find

$$\sqrt[4]{\frac{\pi\alpha_0 r_0 Z^* e^2}{hv}} = \cdot 61,$$

and so (34) becomes

$$\lambda_1 = \frac{\cdot 61}{h} \sqrt{U_0 E}, \quad . \quad . \quad . \quad (36)$$

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* b_1, or more strictly λ_1, must be less than λ, the disintegration constant, as is evident from (39) below, where $\dfrac{N}{N_0} > 1$.

giving for λ_1 about half the value obtained in (19) by the approximate method.

The simple approximate method discussed in Section A does not give any idea of the radius at which the α-particle is emitted. The rigorous treatment given in the present section, however, gives the radius to be $r_0 \sim 1 \cdot 2 \times 10^{-15}$ cm. It is remarkable that r_0 thus determined is independent of the damping coefficient. This should be expected when it is remembered that r_0 of the present theory is the radius of the hard core. It should be noted that beyond r_0 the Coulomb repulsive force $\dfrac{2Z^*e^2}{r^2}$ must act on the α-particle, so that when it goes to infinity, *i. e.*, becomes free, the energy of the α-particles must be *at least* $\dfrac{2Z^*e^2}{r_0}$, where $r_0 \sim 10^{-15}$. But on equating the energy of the α-particle on coming out of the nucleus, from experimental data (using the relation $E = \frac{1}{2}mv^2$) with $\dfrac{2Z^*e^2}{r_0}$, it is found that r_0 is of the order $1 \cdot 4 \times 10^{-12}$. This shows that the experimental value of the energy of the emitted α-particle is less than the minimum value given by the present theory. This apparent discrepancy is very easily explained when we remember that r_0 from our theory is really the radius of the hard core. On coming out of hard core the α-particle enters not a free space, but the spherical shell already filled with polarized helium atoms. These polarized atoms may be considered as loosely bound, like the ions of a solution. So when one α-particle enters the shell, to make room for it another leaves the nucleus from the outer boundary of the shell, which is of the order $r_1 \sim 10^{-12}$, as obtained experimentally. An alternative explanation of the discrepancy may also be suggested. On coming out of the hard core the α-particle collides with the β-particles and the α-particles constituting the polarized helium atoms moving in quantized orbits, and in so doing it excites them, giving up practically the whole of its energy. Thus the actual emission takes place from the outer radius of the nucleus of the order $r_1 \sim 10^{-12}$.

This latter hypothesis may explain the long range emission taking place at some stages of disintegration, when the excited energy is returned to the particle.

It may be mentioned that in a recent paper[*] K. K. Mukherjee has developed a wave-statistical theory of α-scattering which agrees wonderfully with Bieler's experiment and also with the recent experiment of Chadwick at large angles. The theoretical value of r_0 (scattering) obtained by Mukherjee is of the order $\sim 10^{-14}$, being greater than the radius of the hard core ($r_0 \sim 10^{-15}$) obtained by present theory. At small angles of scattering Mukherjee finds that r_0 may be as small as $\sim 10^{-15}$. Rutherford and Chadwick[†] have pointed out that r_0 for small angle scattering by helium is about 1/10 of the value for large angle scattering. It therefore confirms the conclusion reached by Mukherjee. It is needless to point out that r_0 obtained from scattering cannot be less than 10^{-15} and must lie between 10^{-15} and 10^{-12}.

Section C.

In the present section we shall obtain a relation between the well-known disintegration constant and damping coefficient for the hard core already found. Now it follows from the very meaning of the damping coefficient introduced in (2 a) that

$$\lambda_1 = -\frac{1}{N}\frac{dN}{dt}, \qquad \ldots \quad (37)$$

where N is the total number of α-particles inside the hard core. Let us consider a thin shell just inside the core being of thickness Δr_0. Let the number of α-particles in this shell be N_a which may be called the effective number. Thus, if we define the disintegration constant (λ) in the same way as the velocity coefficient of chemical reaction (in the activation theory), we have

$$\lambda = -\frac{1}{N_a}\frac{dN_a}{dt}. \qquad \ldots \quad (38)$$

It is evident that $N = N_0 - N_a$, where N_0 is the number within the shell considered. As N_0 does not change with time, we have

$$\frac{dN}{dt} = \frac{dN_a}{dt}.$$

[*] K. K. Mukherjee, *Phys. Zeitschr.* xxxiv. p. 175 (1933).
[†] Rutherford and Chadwick, Phil. Mag. iv. p. 605 (1927).

Hence from (37) and (38) we find

$$\lambda = \frac{N}{N_a} \lambda_1. \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Substituting for λ_1 from (36), we have for the disintegration constant

$$\lambda = \frac{\cdot 61}{h} \sqrt{U_0 E} . \frac{N}{N_a} . \quad . \quad . \quad . \quad (40)$$

Now from (14), which is valid for the hard core, we have

$$N_a = N . \text{const.} \frac{\sin^2 \alpha r_0}{r_0^2} r_0^2 \Delta r_0. \quad . \quad . \quad (41)$$

Again, at r_0 the solution for inside may be replaced by the solution for outside (it being one of the conditions of continuity). Thus from (24) and (41) we get

$$\frac{N_a}{N} = \text{const. } \cot u_0 e^{2K(2u_0 - \sin 2u_0)} r_0^2 \Delta r_0. \quad . \quad . \quad (42)$$

Hence, combining (40) and (42), we at once get

$$\lambda = \frac{\cdot 61}{h} \sqrt{U_0 E} \frac{C}{r_0^2 \cot u_0} e^{-2K(2u_0 - \sin 2u_0)}, \quad . \quad . \quad (43)$$

where C includes the unknown normalizing factor and Δr_0. Again, combining the unknown constants C, $\sqrt{U_0}$, and the numerical factor into one constant, (43) may be written in the simple form

$$\lambda = C . \frac{\sqrt{E}}{r_0^2 h \cot u_0} e^{-2K(2u_0 - \sin 2u_0)}. \quad . \quad . \quad (44)$$

This is the equation which connects the disintegration constant with the velocity of the emitted α-particle. Like the corresponding formulæ obtained by wave-mechanics (*l. c.*) eq. (44) does not agree in form with the empirical formula suggested by Geiger and Nuttall.

Numerical Calculation.

On taking logarithm to the base 10 the equation (44) becomes

$$\log \lambda = \log C + \tfrac{1}{2} \log E - 2 \log r_0 - \log h - \log \cot u$$
$$- 2K(2u_0 - \sin 2u_0) \times \cdot 4343, \quad (45)$$

where for K the approximate value is taken from (23). Now r_0 is calculated from the general relation (35). The unknown constant $\log C$ for any family of radioactive substances is evaluated by using the known experimental value of λ (emanation). With the value of $\log C$ thus obtained the formula is used to calculate λ for the other members of the same family. The theoretical and the experimental value of $\log \lambda$ for the three families are given in Tables I., II., and III.
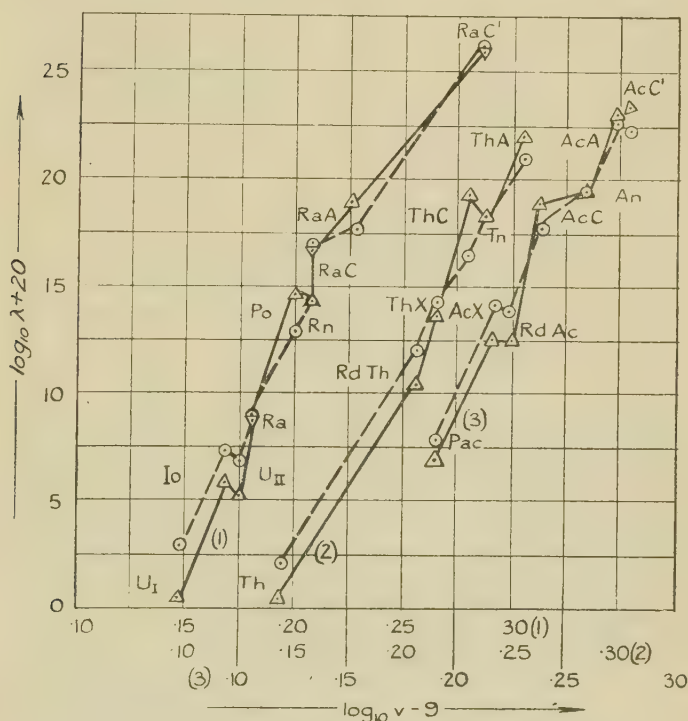
The theoretical and the experimental variations of $\log_{10} \lambda$ with $\log_{10} v$ are shown in the figure with continuous and broken lines respectively for the three families of radioactive substances.

It is evident from the tables that the experimental and the theoretical values of the disintegration constant for different radioactive substances are in good agreement, considering the fact that a slight variation in the value

TABLE I.

Uranium–Radium Family.

Element.	Atomic number.	$v \times 10^{-9}$ cm. per sec.	$r \times 10^{15}$ cm.	$20 + \log \lambda.$ Exp.	$20 + \log \lambda.$ Calc.
U_I	92	1·41	1·122	2·70	0·50
U_{II}	92	1·50	1·122	6·87	5·06
Io..........	90	1·48	1·148	7·38	5·70
Ra	88	1·51	1·174	9·14	8·61
Rn	86	1·61	1·201	14·32	14·32
RaA........	84	1·69	1·231	17·57	18·86
RaC	83	1·61	1·247	16·77	16·48
RaC′........	84	1·922	1·231	25·92	25·63
Po	84	1·58	1·231	12·77	14·64

TABLE II.

Thorium Family.

Element.	Atomic number.	$v \times 10^{-9}$ cm. per sec.	$r \times 10^{15}$ cm.	$20 + \log \lambda.$ Exp.	$20 + \log \lambda.$ Calc.
Th	90	1·39	1·148	2·12	0·51
RdTh	90	1·60	1·148	12·06	10·44
ThX	88	1·64	1·174	14·34	13·52
Tn	86	1·73	1·201	18·10	18·10
ThA........	84	1·80	1·231	20·69	21·62
ThC........	83	1·70	1·247	16·28	19·13

TABLE III.

Actinium Family.

Element.	Atomic number.	$v \times 10^{-9}$ cm. per sec.	$r \times 10^{15}$ cm.	$20 + \log \lambda.$ Exp.	$20 + \log \lambda.$ Calc.
Pac	91	1·55	1·134	7·84	6·96
RdAc	90	1·68	1·148	13·63	12·24
AcX........	88	1·65	1·174	13·85	12·39
An	86	1·81	1·201	19·25	19·25
AcA........	84	1·886	1·231	22·54	22·78
AcC........	83	1·73	1·247	17·73	18·70
AcC′	84	1·9	1·231	22·15	23·06

of v causes an enormous change in λ. A close agreement is also shown by the curves drawn in the figure. It is interesting to note that the curves are all of similar nature, as was to be expected from Geiger-Nuttall empirical relation. The sharp discontinuities are at the elements RaC, ThC, and AcC, all of which give out long-range α-particles.

In conclusion, we may remark that our theoretical formula may be improved upon by considering the nuclear spin.

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Presidency College,
Calcutta, India.
April 1933.

XCII. *A Sodium Glow-lamp.* *By* Prof. F. H. Newman, *D.Sc., A.R.C.S., The Washington Singer Laboratories, University College, Exeter* *.

[Plates XXXIV. & XXXV.]

1. *Introduction.*

WARBURG † first introduced sodium electrolytically into electrical discharge-tubes, using 1000–1200 volts direct current. Burt ‡ made similar experiments with the ordinary type of electric lamp, and found that it was possible to introduce pure sodium into a very high vacuum at a rate as high as one-fourth gram of metallic sodium per hour without the use of high voltage. He found that soda-glass was most suitable, lead-glass being practically useless, so that the sodium ion in the glass must be mobile.

In practice Burt employed a 40 or 60 watt metal-filament lamp from which the base had been removed by heating. The filament was lighted from a 110 volt D.C. source through an adjustable resistance, and the bulb partly immersed in a bath of molten sodium nitrate maintained in a molten condition in an iron crucible. An electrode was also introduced into the molten salt

and connected to the positive lead of the 110 volt D.C. source. The melting-point of the sodium nitrate, $312°$ C., is well below the melting-point of glass, and yet sufficiently high to allow a reasonable electrolytic current to pass through the glass with a small potential drop in the glass. This simple arrangement was not altogether satisfactory, since one end of the filament carried much more current than the other and became overheated, especially if the electrolytic current was as large as 0·1 ampere. Moreover, if the entire bulb gets hot, and so increases the pressure of the sodium vapour, ionization is likely to start between the filament leads, burning them out.

To overcome these faults Burt used series resistances (lamp-bulbs) to limit the ionization currents, and obtained deposits of nearly 300 milligrams of sodium in an hour, using a 60 watt 110 volt lamp, the electrolysis following Faraday's laws, at least to within one part in 500. He also found experimentally that commercial sodium nitrate in the molten state does not attack the glass sufficiently to change the weight of the bulb 0·1 milligram in several hours.

Apparently potassium ions will not pass through the glass. With potassium nitrate instead of sodium nitrate the electrolytic current decreased in only a few minutes, or even less, nearly to zero. If the voltage was maintained at a high value a very small current flowed for a short time, but the glass then fractured. The same applied to lithium nitrate.

Reich * introduced metallic sodium into an argon-glow tube, the latter being of the voltage-regulator type with a constant plate voltage. It was filled with argon at such a pressure as to give an ignition potential of about 100 volts. As in all glow-discharge-tubes the internal resistance of this tube drops to a very low value as soon as discharge takes place, and so necessitates the use of a suitable series resistance, or other current-limiting device, whenever the tube is used in any manner with a current supply capable of delivering more than the maximum current at which the tube is rated. The method of introducing the sodium into the tube was the same as that employed by Burt.

The incandescent-cathode sodium-vapour lamps have recently been developed to such an extent, and the whole

subject of discharge-tube illumination has become so important, that the author has made special tests with sodium-neon and sodium-argon glow-lamps—the ordinary type of beehive-lamp used for illumination purposes—with the idea of obtaining a much simpler type of sodium lamp than those at present in use.

2. *Experimental.*

The argon- or neon-filled beehive-lamps as usually supplied are rated at 5 watts, and contain a ballast resistance in the base to limit the current supplied. The argon-filled lamps used in the present experiments were supplied by the British Thomson Houston Company without any such resistance, because it had been found that the heat from the sodium nitrate bath, during the introduction of the sodium, destroyed the insulation of the resistance, causing a short-circuit when the lamp was operated. The pressure of the argon was 7 mm. of mercury, and the two electrodes were of the familiar type, viz., a spiral and a flat disk. The lamp was lighted from a 210 volt A.C. source through a resistance of 400 ohms—the lamp-current in this case being 0·15 amp.—a value, it will be noted, much higher than the rated value. As the lamp was run continuously at this rating for over an hour without any damage, it is evident that the current, provided that it is not too large, may be considerably greater than that specified without appreciably affecting the phenomena described. The bulb was partly immersed in a bath of molten sodium nitrate, maintained molten in a small copper bath (a calorimeter) by means of a Bunsen flame. A copper-wire electrode was introduced into the molten salt and connected to the positive terminal of a 105 volt D.C. supply through a resistance of about 650 ohms. The negative terminal of the supply was connected to one of the lamp lead-in wires. The resistance can be varied within wide limits, and may even be dispensed with altogether. Under these conditions the current through the sodium nitrate and lamp was 40 milliamperes. To lessen the danger of the bulb fracturing on immersion in the bath the bulb was suspended over the bath while the latter was being heated, so that before immersion the lamp was approximately at the temperature of the bath. Although various bulbs have been immersed many times no case of fracture

has occurred. After completion of the deposit the bulb is of course removed from the bath while the sodium nitrate is in a molten condition. The temperature of the bath was maintained between 315° C. and 340° C., no special precautions being taken to keep it at any one fixed temperature.

With this arrangement, on lighting the lamp and passing direct current through the bath a yellow glow immediately appears in the bulb and bubbles of gas arise from the molten nitrate, due to electrolysis. This glow becomes very intense after a very short time interval —a matter of seconds—the whole of the bulb becoming filled with sodium radiation. The argon radiation is almost completely masked even in the neighbourhood of the spiral electrode. After the electrolysis has continued for some time a bright deposit forms on that part of the lamp which is not immersed in the bath, this deposit becoming thicker with the course of time. For example, 0·0229 gm. of sodium was introduced into the bulb in forty minutes, the electrolysis current being 40 milliamperes. This gives the electro-chemical equivalent of sodium equal to 0·0002385 gm. per coulomb, a value agreeing extraordinarily well with the accepted one. There is no doubt therefore that the effect is due to an electrolytic process. The intensity of the sodium radiation depends upon the electrolytic current ; with 17 milliamperes it was approximately six times that emitted by the common Bunsen burner salt-flame.

After the bulb has received a sodium deposit it can be used as a source of D line radiation. The lamp is connected directly to the 210 A.C. or D.C. mains through a resistance of about 500 ohms. On first starting the lamp the characteristic argon radiation is emitted, but as it warms up the argon lines become fainter and practically disappear, leaving only the D lines of sodium. The latter are intense and narrow. No external heating is required, but if the lamp is enclosed in a small electric heater or heated carefully by means of a Bunsen flame the D lines become more intense. The introduction of sodium into the lamp in such a small quantity that it cannot be detected on the walls is sufficient to give the sodium radiation when the lamp glows, the argon lines being very faint. After continual use the glass shows no brown coloration such as is usually experienced

when an electrical discharge is passed through sodium vapour, and on cooling there seems to be no deposition of the sodium on the clear parts of the lamp—at least the deposit cannot be observed and does not interfere with the transmission of light.

The appearance of the glowing sodium lamp is shown in the photographs reproduced in Pl. XXXIV. In (*a*) the electrolytic current is passing through the bath with the lamp glowing, whereas in (*b*) there is no electrolytic current although the lamp is lighted. It will be noted that in the former case the sodium glow is diffused more or less uniformly throughout the bulb, whereas in (*b*) the glow is concentrated in the neighbourhood of the electrodes. A spectrogram of the radiation near the glass walls in case (*b*) shows only the two D lines, which suggests that in this location there is resonance radiation of the sodium vapour, produced by the radiation from the electrical discharge between the two electrodes, since a spectrogram of the light in the neighbourhood of the electrodes does show faint traces of the sodium subordinate series lines in addition to the more intense D lines.

The spectrograms are shown in Pl. XXXV. In (*e*) the spectrum of the radiation emitted when the electrolytic current passes through the nitrate bath shows some trace of the subordinate series lines of sodium, but they are missing when the lamp is glowing in the absence of this current. A study of these spectrograms indicates that, with proper choice of the part of the lamp used for a source, light may be obtained in which the argon spectrum is missing, or is very faint, and in which the D lines appear with intensity sufficient for calibration or comparison purposes.

The introduction of the sodium into the bulb is explained in a manner somewhat similar to that put forward by Burt. The negative ions produced by the electrical discharge are driven to the inner surface of the glass walls by the unidirectional applied electric field. These ions neutralize the sodium ions in the glass, which thus become atoms. These in turn are evaporated by the heat and condense on the upper cooler portion of the lamp. Sodium ions from the molten sodium nitrate replace those of the glass and migrate through the latter, being in turn neutralized at the inner surface. Thus sodium passes electrolytically through the glass wall.

In a similar manner sodium can be introduced into a neon-filled lamp, but the glow in this case is not such a satisfactory source of D line radiation, since there are numerous neon lines in the neighbourhood of the D lines, and their luminosity remains appreciable even when the sodium glow is present.

This method of introducing sodium into a neon-filled lamp can also be applied for photoelectrical purposes. One of the midget type of neon lamps was utilized, and a layer of sodium deposited on the disk-shaped electrode. The lamp then acted as a photoelectric cell, and worked very satisfactorily when used to compare intensities of radiation.

XCIII. *On the Variation of the Inter-electrode Capacity of a Triode at High Frequencies.* By BHABANI CHARAN SIL, *M.Sc., Station Engineer, Indian State Broadcasting Service (formerly Khaira Research Scholar, Calcutta University)* *.

Introduction.

DURING recent years a large number of experiments have been made to furnish experimental evidence of the Eccles-Larmor theory of the reduction of dielectric constant of a space containing charged particles, which has been so fruitful in explaining the bending of the electromagnetic waves by the ionized upper atmosphere. All the experiments heretofore tried aim at determining the capacity of a condenser the space between the plates of which is filled with ions or electrons or both. These experiments may broadly be divided into two classes— one, in which the electrons and ions are produced by electrical discharge at low pressure [1], [2], [3], [4], and the other in which only electrons are present in a space so highly rarefied that the collision of the electrons with gas molecules can be neglected [5], [6]. Both types of experiments have been found to yield rather conflicting results. The sense of the change of the dielectric constant is found sometimes the same as and sometimes the opposite to that predicted by the Eccles-Larmor

theory. Often no change is recorded. In other words, the capacity of a condenser containing charged particles between its plates is sometimes found to be greater, sometimes less, and sometimes equal to the capacity when the space is empty of charged particles. In case of experiments with ionized gas a fairly satisfactory explanation of the anomalous result obtained is given by supposing that ionic sheaths are formed on the surface of the condenser plates immersed in the gas ionized by electric discharge [3]. The sheaths have the effect of increasing the capacity of the condenser by reducing the effective distance between the plates. In the second case—that of pure electronic atmosphere—which is most conveniently obtained by heating a metal in a vacuum, experiments by Benham [5] and Bergman & Düring [6] show that the dielectric constant is reduced to a value of less than unity by the presence of the electrons. In Benham's[5] investigation the measurement is made on the capacity of a condenser system one of the plates of which is hot. In Bergman and Düring's [6] experiment the electrons are drawn from the hot plate by a positive grid placed near it, and the dielectric constant is measured of the space between the grid and another plate parallel to it.

In the course of an investigation on the high frequency resistance of thermionic valves, recently published in this Journal [10], we noticed that with an arrangement somewhat similar to that of Bergman and Düring [6] an increase of dielectric constant of the plate-grid space of a triode valve is recorded under certain experimental conditions. These observations were followed up, and the present communication is on a study of the conditions under which one would expect to record either an increase or a decrease in the dielectric constant.

Experimental Arrangement.

It would be easier to follow the theoretical discussion in the next section if the experimental arrangement and the results obtained are described first. The essential of the method is to determine the capacity of the condenser formed by the plate and the grid of a triode with the help of a Lecher system once when the filament is cold and again when it is hot, the electrons emitted in the latter

case being drawn into the plate-grid space by the application of a positive potential on the latter.

The valve used was Osram T 15; the cap and base were removed to minimize the capacity of leads. The plate and grid were connected to a Lecher wire-system made of no. 18 bare copper wire, distance 5·2 cm. between the wires excited by the oscillator O (fig. 1). The bridge consisted of a stout copper wire with a fixed condenser of value ·01 mf. in its middle, as shown in fig. 1. The Lecher wire connected to the grid was connected at its bridged end with the filament through a battery of 50 volts. (This was the maximum voltage used, because a higher voltage had a tendency to produce Barkhausen & Kurz oscillations.) The electrons emanating from the filament thus accelerated found their way into

Fig. 1.
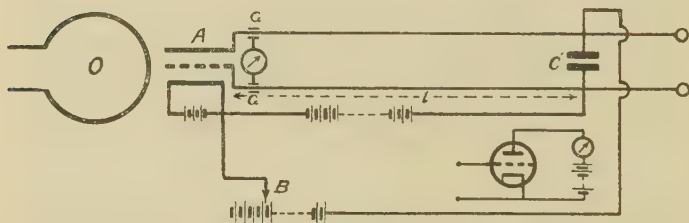
The inset shows the diagram of valve-voltmeter.

the grid-plate space of a valve ; here they were subjected to a field the strength of which was determined by the magnitude of the voltage applied to the plate by the battery B. The condenser C′ in the bridge prevented short circuiting of the grid or the anode battery. The positions of resonance were observed with a thermionic voltmeter placed near the input end A. The diagram of the voltmeter is shown in the inset ; GG are narrow glass tubes insulating the voltmeter leads from the Lecher wires. The experimental procedure was to work the oscillator and to observe the length of resonance by noting the position of the bridge for which the thermionic voltmeter gave minimum deflexion, first when the filament battery was off and again when it was on. To obtain greater precision regarding the length l of resonance, curves were usually plotted showing deflexions of the thermionic voltmeter against the positions of the

bridge. Such curves were specially useful when the tuning was flat. A few typical curves are shown in fig. 2.

Fig. 2.

Curve 1 - Filament cold.
Curve 2 -   ,,   hot, plate -4V.
Curve 3 -   ,,   ,,, plate +4V.
Frequency - 11540 kc/sec.

Voltmeter deflection.

Distance of the bridge in cms.
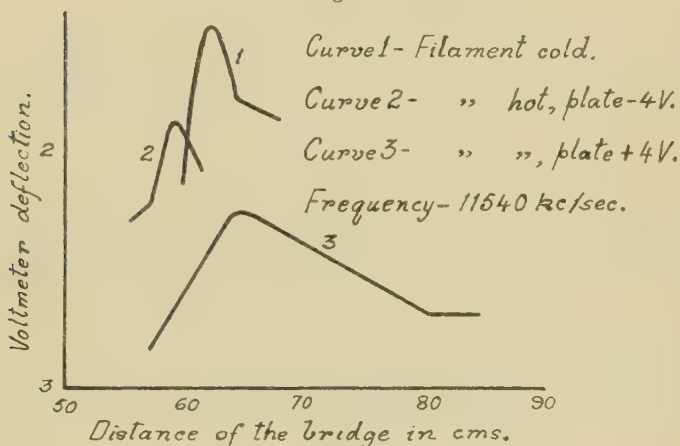
Percentage change of plate-grid capacity of Osram T 15.
Filament 6 volts.   Grid 50 volts positive.

Plate voltage. Frequency in kilocycles.	−20	−8	−4	0	+4	+8	+16
11538·4 (26 m.)	No change	—	+8·6%	Very flat tuning	−5·2%	—	No change
23076·9 (13 m.)	No change	+4·4%	+5·8%	Very flat tuning	−3·4%	−0·6%	No change
57653·8 (5·2 m.)	No change	+3·1%	+4·0%	Very flat tuning	−2·5%	−0·5%	No change

Positive sign indicates an increase, and negative sign a decrease of the plate-grid capacity.

The change in the value of the capacity when the filament was lighted could be easily calculated by noting the change in the position of the bridge. Thus if l_1 and l_2 are the "hot" and the "cold" resonant lengths of

the bridge, then the percentage change in the value of the capacity is given by

$$\frac{\cot\dfrac{2\pi}{\lambda}\,l_2-\cot\dfrac{2\pi}{\lambda}\,l_1}{\cot\dfrac{2\pi}{\lambda}\,l_1}\times 100$$

(see equation 5).

Theoretical Discussion.

We can best begin by giving a brief treatment of the theory of the reduction of the dielectric constant brought

Fig. 3.
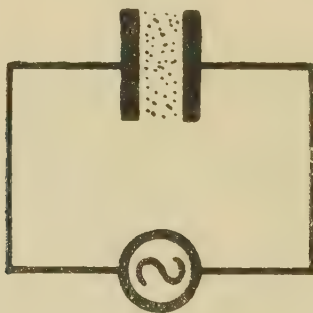
about by the presence of charged particles according to Eccles-Larmor [7], [8].

If an alternating electric field

$$f = \mathrm{F}\sin pt$$

is applied between the two plates of a condenser (fig. 3), having N ions per unit volume, then, supposing e and m to be the charge and the mass of one ion, the equation of motion of each ion in the direction of the field is

$$m\,\frac{d^2x}{dt^2} = fe = \mathrm{F}e\sin pt.$$

The velocity produced by the field is therefore given by

$$\frac{dx}{dt} = -\frac{\mathrm{F}e}{pm}\cos pt.$$

There must therefore be a conduction-current density

$$\mathrm{N}ev = -\frac{\mathrm{FN}e^2}{pm}\cos pt,$$

where
$$v = \frac{dx}{dt}.$$

The Maxwell displacement-current density in the absence of ions is

$$\frac{1}{4\pi}\frac{df}{dt} = \frac{1}{4\pi}\mathrm{F}p\cos pt.$$

Hence we see that, due to the presence of the ions, the total current density changes from

$$\frac{\mathrm{F}}{4}p\cos pt \text{ to } \left(1 - \frac{4\pi\mathrm{N}e^2}{p^2m}\right)\frac{\mathrm{F}p}{4\pi}\cos pt, \quad . \quad . \text{ (1)}$$

or, in other words, the presence of ions has reduced the effective dielectric constant of the medium by

$$\frac{4\pi\mathrm{N}e^2}{p^2m}.$$

If N is so large that $\dfrac{4\pi\mathrm{N}e^2}{p^2m}$ is greater than unity.

i. e., if the dielectric constant is negative, then the resultant current through the condenser lags $\pi/2$ behind the voltage. The capacity now behaves like a self-inductance.

In this simple theory there is no room for recording a dielectric constant greater than unity.

In deducing the above formula by considering the idealized case of an electron atmosphere uniformly distributed between the plates we have tacitly made two assumptions. These are :—

(i.) The electron distribution between the plates is uniform, and remains so even when the alternator is switched on, the electrons merely swinging about their mean position. Thus the only alternating force acting on the electron is that due to the electric field produced by the alternating voltage applied to the plates.

(ii.) Each electron remains for an indefinite period between the condenser plates—that is, there is no absorption of electrons by the condenser plates.

In actual experimental conditions neither of these assumptions is fulfilled, but still certain simplifying assumptions can be made for the case where the electrons are obtained by thermionic emission in high vacuum. Let us consider the assumptions one by one.

If one of the condenser plates is heated then the electrons emitted are mostly concentrated near the surface of the plate and the distribution is far from being uniform. It is estimated that for emission from tungsten at a temperature of 2400° absolute the density falls to ·0043 per cent. of its value at the surface at a distance of only ·2 cm. A more or less uniform distribution can be produced by drawing the electron cloud towards the cold plate by applying a positive potential to the latter [8], as has been shown by Rakshit [11].

In our experiment a triode valve was used, and in this case a fairly uniform distribution is obtained by applying a high positive potential to the grid (with respect to the filament) and allowing the electrons to enter the condenser formed by the grid and the plate through the mesh of the grid. If the plate is at the same potential as that of the grid the electrons will be moving in a field-free space and there will be a uniform distribution. However, for reasons to be discussed later, measurements were taken with a potential of the plate much less than that of the grid. The distribution is much less uniform in this case.

Another consequence of assumption (i.) is that the effect of the space charge is neglected. An electron situated, say, close to the left-hand plate (fig. 3) is acted upon by two forces, one due to the applied voltage on the plates and the other due to the electron cloud situated on the right of the point. It is assumed that the alternating voltage applied to the plates does not alter the density of the distribution, and equation (1) holds good because the force on the electron due to the space charge does not alter with time.

The necessity of assumption (ii.) is evident if we note that in order that equation (1) may be applicable it is necessary that each electron should remain between the plates for a period large compared with the period of the oscillatory voltage applied to the plates. If the time of stay is small compared with the period of the alternating force, then the contribution of each electron

to the conduction current is necessarily small, and the amount of the reduction of the dielectric constant is also diminished. These points have been clearly explained in a paper by Benner[9], and we quote here his formulæ:

$$\sigma = \frac{Ne^2}{mp^2T}(1-\cos pT) \quad . \quad . \quad . \quad . \quad (2)$$

$$\Delta\epsilon = -\frac{4\pi Ne^2}{mp^2}\left(1-\frac{\sin pT}{pT}\right). \quad . \quad . \quad (3)$$

Here σ is the conductivity and $\Delta\epsilon$ is the change in the dielectric constant brought about by the presence of electrons of density N between the condenser plates; T is the time which elapses between the entry and the exit (or absorption by the plate) of an electron into and from the region between the condenser plates.

In our experiment therefore the condenser formed by the plate and grid of the triode had a medium of which the dielectric constant was given by equation (3) and conductivity by (2). Let us consider how such a condenser would behave when connected to one end of the Lecher system. Let C_0 be the value of the plate-grid capacity in the absence of the electrons. Then, if L and C are the inductance and capacity per unit length of the Lecher system, we have

$$z = j\sqrt{\frac{L}{C}}\tan\frac{2\pi}{\lambda}l - \frac{j}{pC_0}, \quad . \quad . \quad . \quad (4)$$

where z is the impedance of the line as measured at the input end due to a length l of the wires. If resonance is established by moving the bridge, then, since z is zero,

$$\sqrt{\frac{L}{C}}\tan\frac{2\pi}{\lambda}l = \frac{1}{pC_0}. \quad . \quad . \quad . \quad (5)$$

Now if electrons are let in they will produce a twofold effect: firstly, the dielectric constant will be reduced, and, secondly, the space between the condenser plates will become conducting. The former will cause the resonance point to move away from the input end, *i. e.*, the length l will increase. The latter, it might seem at first sight, would cause no change of the resonance point, because we are measuring the "voltage resonance," and it is well-known that in an oscillatory

circuit, consisting of inductance, resistance, and capacity, the voltage resonance. *i. e.*, the frequency at which the voltage across the condenser attains a maximum value, remains unaffected by the condenser dielectric acquiring conductivity ; it is only the current resonance, *i. e.*, the frequency at which the current in the circuit attains a maximum, is affected by a conductivity of the condenser dielectric [3].

It should, however, be remembered that the voltage resonance condition holds only when the conductivity of the dielectric is uniform. If it is non-uniform, for instance, if the space between the condenser is divided into two halves by an imaginary plane parallel to the plates, and if one half only of the dielectric acquires a conductivity, then the voltage resonance condition no longer holds. The conductivity of the one half will alter the resonance frequency at which the voltage across the condenser attains a maximum when the dielectric is not conducting. In fact the conductivity of only a portion of the dielectric will tend to increase the effective capacity of the condenser. Thus we see that when the conductivity acquired is not uniform along the distance d separating the condenser plates, the effect of equation (2) will be to increase the resonance length l of the Lecher system, and that of equation (3) to decrease the same. The actual shift of the resonance point is determined by the relative magnitudes of these two factors.

Now an inspection of equation (3) shows that an appreciable reduction of the dielectric constant is possible only when $\dfrac{\sin p\mathrm{T}}{p\mathrm{T}}$ is small compared with unity, or, in other words when $p\mathrm{T}$ is large compared with unity, the maximum value of $\dfrac{\sin p\mathrm{T}}{p\mathrm{T}}$ being 1. $p\mathrm{T}$ can be increased by increasing p or T or both. A large increase of p is not desirable because it diminishes the expression outside the brackets ; it is therefore advisable to increase T. We thus see that the most favourable condition for registering a decrease of dielectric constant is on the one hand to have the electron distribution uniform, and on the other hand to make the time of stay of electrons T between the condenser plates large. The first condition can be secured by raising the voltage of the plate to the

same value as that of the grid. The electrons entering the grid-filament space through the grid-mesh then move with uniform velocity, and have therefore uniform density throughout the entire region of the condenser space. The second condition, on the other hand, is secured by keeping the plate at a potential lower than that of the grid. The electrons will then be moving in a retarding field, and will be made to stay much longer between the condenser plates. We have thus two opposing conditions, but it can be shown that the second one has a preponderating effect. This is seen if expressions (2) and (3) are expanded in series. These can be written as

$$\sigma = \frac{Ne^2}{m}\frac{T}{2!},$$

$$\Delta \epsilon = -\frac{4\pi Ne^2}{m}\frac{T^2}{3!},$$

with sufficient approximation if $\frac{\sin pT}{pT}$ is less than

unity. It is therefore seen that if T is increased the proportionate increase of the numerical value of $\Delta\epsilon$ is greater compared with the proportionate increase of σ. It is therefore advantageous to increase the time-period T, though this involves an increase of σ (perhaps in a non-uniform manner) when it is desired to record a decrease of the dielectric constant.

The numerical calculations in the next section will make these considerations clear.

Discussion of the Results.

Grid voltage 50. The velocity of the electrons when passing through the grid is given by

$$\tfrac{1}{2}mv^2 = eV,$$

or $\qquad\qquad v = 4\cdot20 \times 10^8$ cm./sec.

The distance between the grid and plate being $\cdot30$ cm., $T = \cdot71 \times 10^{-9}$ sec. if the electrons move with uniform velocity from grid to plate. The frequencies used varied between $6\cdot00 \times 10^7$ and $1\cdot00 \times 10^7$ cycles per second; pT therefore varied between $\cdot267$ and $\cdot045$; the values of $\frac{\sin pT}{pT}$ are $\cdot984$ and $\cdot999$ respectively. Thus according

to equation (3) no appreciable change of the dielectric constant should be noticed, since the expression within brackets is practically zero. This is what we have actually observed. In fact the table shows that a voltage on the plate $+16$, which is much lower than that on the grid, fails to record any change in the dielectric constant, because $\dfrac{\sin \mathrm{T}p}{p\mathrm{T}}$ is nearly equal to 1. The increase was not recorded because the electron distribution was practically uniform with this voltage on the plate.

Now T can be increased by applying a potential on the plate equal to that of the filament, so that the electrons are just brought to rest near the surface of the plate. With the grid voltage the same as before, and the plate connected to the filament, the electrons will now take double the time to move from grid to plate, *i. e.*, $p\mathrm{T}$ is now $\cdot534$ and $\dfrac{\sin p\mathrm{T}}{p\mathrm{T}}$ is $\cdot953$. Even now the fraction is not very different from unity. A more detailed calculation [10] of the time of transit, taking into account the cylindrical shape of the electrodes, gives $\mathrm{T} = 3\cdot30 \times 10^{-9}$ sec.; $p\mathrm{T}$ is then equal to $1\cdot244$ and $\dfrac{\sin p\mathrm{T}}{p\mathrm{T}}$ is $\cdot761$. For some of the electrons at least T will be $2 \times 3\cdot3 \times 10^{-9}$ sec., because they will take an equal time to return from the plate surface to the grid, and will thus remain between the plate-grid space for double the time. It will be seen from the table that a decrease in the capacity has been obtained when the plate is nearly ($+4$ volts) at the same potential as that of the filament.

Finally, let us consider the effect of making the potential of the plate lower than that of the filament. The retarding field between the grid and the plate will now be so strong that the electrons coming out of the grid will be unable to reach the plate. The electrons will now fill only a portion of the space between the condenser plates ; this portion of the condenser will therefore acquire a finite conductivity, while the other portion, devoid of electrons, will have zero conductivity. This non-uniform distribution of conductivity will cause an increase in the effective capacity of the condenser.

The " physics " of this effect will perhaps be better understood from the following considerations. In fig. 4

the left half of the condenser contains electrons, while the right half is empty. Suppose, in the first instance, that the electrons are rigidly fixed in space : at the point P the electric intensity at any instant will be due partly to the instantaneous voltage V applied to the plates by the alternator and partly to the force exerted by the electron cloud situated on its left, which is given Poisson's equation

$$\frac{d^2V_P}{dx^2} = 4\pi\rho.$$

When the alternator works the intensity at P undergoes fluctuations, and a displacement current $|\frac{1}{4\pi}\frac{df}{dt}$ flows

Fig. 4.
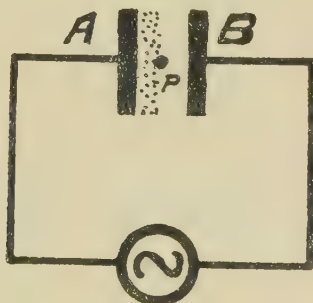
per unit area across it. Now this displacement current is constant throughout the entire region of the condenser, because, though the total force is different at different points along d, due to the effect of the space charge, yet the rate of fluctuation of the force with time is the same at all points, being due only to the fluctuations of the alternator voltage, and not due to the space charge, which is fixed in space.

Next suppose that the electrons are free to move, and consider again the intensity at P. Suppose that at a particular instant the alternator is increasing the voltage of plate B (fig. 4). This will tend to increase the intensity at P, but the increasing voltage on B will, at the same time, drag the electron cloud towards the right of the point P. This portion of the electron cloud will tend to produce an intensity at P the sense of which

will be opposite to that produced by the increase of the voltage of B. Thus the resultant intensity f' will change less rapidly with time, due to the combined effect of the variation of voltage of the alternator and the movement of the space charge, and the amplitude of the displacement current will decrease. This decrease will be more and more pronounced as we proceed from B to A. We might then regard points situated inside the space

Fig. 5 *a*.
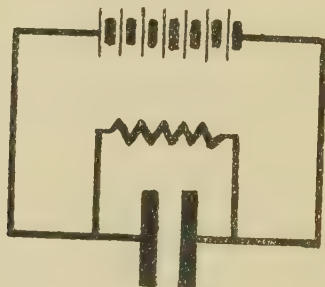
Fig. 5 *b*.
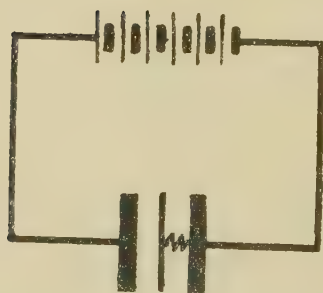
charge as being shielded from the fluctuating electric field produced by the alternator, as if the space charge were a conducting medium.

Perhaps the simplest way of understanding how a non-uniform distribution of the conductivity brings about an increase in the effective capacity is to consider the case when a steady field is applied between the plates. In fig. 5*a* the conductivity of the medium between the condenser plates is represented by a shunting resistance. In fig. 5 *b* the non-uniform conductivity is represented by

a resistance shunting only a portion of the medium between the plates. In fig. 5 *a* there will be a voltage drop V_0 across the condenser, due to the current flowing through the resistance, and the condenser will take up a charge appropriate to this voltage, $Q = CV_0$. In fig. 5 *b*, on the other hand, no current is flowing, and as far as the steady field is concerned the effect is as if the right-hand condenser were absent. The effective capacity is thus only that due to the left-hand condenser the capacity of which is greater than that of the two condensers in series.

The table shows that the increase in capacity is noticed only when the plate is at a lower potential than that of the filament, because in this case the non-uniformity of the electron distribution is greatest. When the negative voltage on the plate is greatly increased the space charge is confined in a narrow region near the grid, and the non-uniformity effect is again decreased and no change in capacity is recorded. With a large negative voltage T is also decreased, making the effect of either σ or $\Delta \epsilon$ inappreciable.

The whole phenomena of the increase and the decrease of the plate-grid capacity of the condenser noticed by us are summarized in the conclusion below.

Summary and Conclusion.

Measurements have been made on the " hot " and the " cold " capacity between the grid and the plate of a triode with the help of a Lecher system. It is found that when an accelerating voltage is applied to the grid to draw the electrons from the hot filament into the space between the grid and the plate the effective value of the capacity undergoes changes the sense and the magnitude of which depend upon the voltage of the plate with respect to the filament.

Results obtained are classified thus :—

(1) Plate voltage slightly higher than that of the filament. Hot capacity is lower than the cold capacity.

(2) Plate voltage a little lower than that of the filament. Hot capacity greater than cold capacity.

(3) Plate voltage, (*a*) much higher (nearly same as that of the grid) or (*b*) much lower (nearly as much as

the grid is higher) than that of the filament. No difference between hot and cold capacity.

(1) is explainable by the Eccles-Larmor Theory; (2) is explained by the fact that the distribution of the electrons between the condenser plates is in this case of a non-uniform character ; (3 *a*) is explained by the time of stay of the electrons between the condenser plates being reduced to a value small compared with the period of the measuring oscillations (Benner)[9]; (3 *b*) is explained as due partly to the same cause as (3 *a*) and partly to the fact that the electrons are confined in a narrow region near the electrodes and factor (2) is inoperative.

The investigation was undertaken at the suggestion of Prof. S. K. Mitra, D.Sc., and I take this opportunity of thanking him for his helpful interest and advice during the course of the work.

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XCIV. *The Strain Energy of an Elastic Bar : a useful Transformation. By* E. H. BATEMAN, *M.A.**

IN the analysis, by Castigliano's method of minimum strain energy, of a plane elastic network formed of bars connected to one another at their ends, the indeterminate quantities may be the bending moments in the bars at these points. If these moments at the ends of any bar be denoted by α, β, and if there are no other

* Communicated by the Author.

forces producing flexure, the strain energy, W, in the bar is given by

$$6EKW = \alpha^2 + \alpha\beta + \beta^2,$$

where E is Young's modulus and K is the rigidity of the bar.

If the bar carries any form of transverse load distribution, and α, β are again the actual end moments, the strain energy is given by

$$6EKW = \alpha^2 + \alpha\beta + \beta^2 - \alpha(2a + b) - \beta(2b + a) + C,$$

where a and b are the end moments which would be produced in the bar by the applied transverse loads if the ends were fixed in direction, and C represents all terms which are independent of α, β.

The values of a and b can easily be written down in most cases which are likely to occur, and they can be quickly estimated for load distributions which do not submit to simple analysis.

The strain energy can therefore be stated in terms of the indeterminate quantities without formulating and operating on a general expression for the bending moment at any point in the bar.

The proof is as follows :—

(i.) When the bending moment m at any point in the bar is determined simply by the values of α, β, we have

$$m = \alpha\left(1 - \frac{x}{l}\right) + \beta\frac{x}{l}, \quad . \quad . \quad . \quad . \quad (1)$$

where l is the length of the bar and x the coordinate of the point;

the strain energy, $\displaystyle W = \int_0^l \frac{m^2\, dx}{2EI}$,

where I is the moment of inertia corresponding to the plane of bending, and we find

$$2EIW = \alpha^2\frac{l}{3} + \alpha\beta\frac{l}{3} + \beta^2\frac{l}{3},$$

or $$6EKW = \alpha^2 + \alpha\beta + \beta^2,$$

where $$K = I/l.$$

(ii.) When the bar is acted on by transverse loads and the end moments are α, β, the moment at any point in

the bar may be expressed in the form $M = m + M'$, where m is the moment due to the end moments alone as defined in (1) and M' is the moment due to the transverse forces acting alone and balanced by the necessary end reactions.

If, now, a and b are the end moments which would be produced by the transverse load system alone if the ends of the bar were fixed in direction, a and b are determined by Mohr's equations

$$\int_0^l (M' + m')\, dx = \int_0^l (M' + m')x\, dx = 0, \quad . \quad . \quad (2)$$

where
$$m' = a\left(1 - \frac{x}{l}\right) + b\frac{x}{l}. \quad . \quad . \quad . \quad (3)$$

The bending moment at any point in the bar may now be written

$$M = (m - m') + (M' + m'),$$

and the strain energy

$$2EIW = \int_0^l M^2\, dx = \int_0^l (m - m')^2\, dx + \int_0^l (M' + m')^2\, dx$$
$$+ 2\int_0^l (m - m')(M' + m')\, dx.$$

Then, since $(m - m')$ is of the form $(A + Bx)$,

$$\int_0^l (m - m')(M' + m')\, dx$$

may be expressed in the form

$$A\int_0^l (M' + m')\, dx + B\int_0^l (M' + m')x\, dx,$$

which by (2) is equal to zero.

Hence,

$$2EIW = \int_0^l m^2\, dx - 2\int_0^l mm'\, dx + \int_0^l m'^2\, dx$$
$$+ \int_0^l (M' + m')^2\, dx. \quad . \quad (4)$$

But $\displaystyle\int_0^l mm'dx = \int_0^l \left(\alpha - \overline{\alpha - \beta}\frac{x}{l}\right)\left(a - \overline{a - b}\frac{x}{l}\right)dx$

$$= a\alpha \cdot \frac{l}{3} + b\beta \cdot \frac{l}{3} + (a\beta + b\alpha)\frac{l}{6},$$

or $\displaystyle \frac{2}{l}\int_0^l mm'dx = \alpha \cdot \frac{2a+b}{3} + \beta \cdot \frac{2b+a}{3}.$

Thus (4) may be written

$$6\text{EKW} = \alpha^2 + \alpha\beta + \beta^2 - \alpha(2a+b) - \beta(2b+a) + \text{C},$$

where C represents the terms which do not contain α, β.

XCV. *The Heights of Nuclear Potential Barriers.*   By
E. Watson Pollard, *Ph.D., Assistant Lecturer in Physics at the University of Leeds* *.

Introduction.

IT is now well known that the interpretation of the phenomena of the nucleus requires a potential barrier of the type suggested by Gurney and Condon and Gamow. At large distances from the nucleus this potential barrier is due to the Coulomb repulsion, while at very close distances this gives way to an attractive force whose nature is not definitely known, but which probably depends on the distance from the nucleus to a high inverse power ; thus scattering experiments have been made to agree with an inverse fourth or fifth power. As a result of the superposition of these two fields of force there will be a maximum potential at a certain distance from the centre of the nucleus ; this is called the height of the nuclear barrier. In recent years the work on artificial disintegration and on the scattering of alpha particles by light nuclei has made available a range of experimental evidence on the heights of nuclear barriers ; it is the aim of this paper to collect this evidence, and show how it suggests a simple general rule for the light nuclei. An attempt will be made to reconcile the experimental findings with nuclear theory, which predicts such a rule with remarkable simplicity, although at the same time

numerical discrepancies remain between two lines of evidence.

The cloud-chamber experiments of Blackett show that the alpha particle enters a nucleus which it disintegrates ; in some cases this entry takes place through the potential wall, as, for example, aluminium, at a level of energy equal to a virtual alpha particle level inside ; in other cases, as, for example, nitrogen, the entry is over the top of the barrier. With a radioactive source giving fast enough alpha particles both methods can take place for the same element. Such alpha particles, on entering the nucleus, give rise to disintegration products (whether protons, or neutrons, or gamma-ray quanta) which can be detected by suitable methods, and if we select a group of such products which is known to be caused by the entry of the alpha particle over the top of the barrier we can find the shortest range alpha particle which will give any disintegration. The energy of this alpha particle will be the energy of the top of the barrier. Such experiments have been carried out by different workers on different elements either directly or indirectly, but, except in a few cases, they have not carried the deduction to the point of fixing the actual barrier height, perhaps because there has been no justification in each single experiment for such interpretation of their results. In addition to this evidence from nuclear disintegration there has been valuable work on alpha particle scattering which shows the region within which anomalous scattering is appreciable—that is, the region approximating to the top of the potential barrier ; this work, linked with the former, gives a total of seven elements for which we have some positive information. There is a third source of evidence which will shortly be of great value—evidence from disintegration by fast hydrogen ions. Here penetration of the barrier is much easier than for alpha particles, and the sources used much stronger, so that the strict minimum energy cannot be found. There is, however, an energy past which the yield of disintegration products from a thick layer rises linearly with the applied voltage ; this energy is most probably the top of the potential barrier. A systematic investigation of the elements in this way will not be difficult and will yield most important results.

The collection of the information from the various sources, as described below, has shown that these barrier

heights appear to vary regularly in a surprisingly simple manner ; and although the evidence available is by no means conclusive, nor its interpretation free from hypothesis, yet it is clearly worth while to focus attention in the disintegration experiments on the critical energy of the impinging particles, in order to confirm the rule suggested by this collective consideration of the data. A preliminary account of the rule obtained has appeared elsewhere *.

More Precise Meaning of the Height of a Barrier.

If the alpha particle were not governed by the wave equation there would be a precise meaning to the height of a barrier ; as it is, alpha particles can penetrate through the barrier below the top, so that there will still be a measurable yield of products when the incident energy is too small to scale the maximum. The transparency of a barrier is governed partly by a term of the type

$$e^{\frac{4\pi}{h}\int [2m(\mathrm{V-W})]^{1/2}dr},$$

where m is the mass of the particle, V the potential of the top of the barrier, W the energy of the alpha particle. The chance of penetration of an alpha particle therefore diminishes rapidly as W becomes less, so that in practice there is a fairly sharp drop in the number entering the nucleus when their energy falls below that of the top, which means a drop in the number of disintegration products. Since the experiments give evidence as to the energy at which the particles or quanta cease, it seems simplest to take the region below the top of the barrier at which penetration becomes too small to observe rather than the actual barrier height, about which experiment does not yield direct information. The corresponding region in the case of the scattering experiments will be that in which the anomalous nature first becomes definite. There is therefore an uncertainty about the actual meaning of a barrier height which must not be lost sight of in reckoning the value of the experimental evidence.

In disintegration by fast hydrogen ions the same expression for transparency holds. In this case the number of primary ions available is so large that the yield

* E. Pollard, ' Nature,' cxxxi. p. 97 (January 21st, 1933) ; cxxxi. p. 398 (March 18th, 1933).

of disintegration products continues well below the level of the top. There is, however, an energy above which the yield ceases to rise ; this will presumably be the true top of the potential barrier.

Evidence from Minimum Energy Experiments.

Direct evidence in which the yield of the disintegration product is plotted against the energy of the incident alpha particle is available for the elements nitrogen, lithium, fluorine, beryllium, and boron. Of these the only wholly satisfactory element is nitrogen, for which the work of Rutherford and Chadwick *, confirmed by Pollard †, indicates the minimum effective alpha particle energy to be $4 \cdot 2 \times 10^6$ electron volts. The work of Webster ‡ on the artificial quanta from lithium shows there is a minimum alpha particle range of approximately $1 \cdot 5$ cm., which gives a value of $2 \cdot 83 \times 10^6$ electron volts for the barrier height. This is not entirely satisfactory, since the yield from lithium was not very large. Fluorine has been found by Chadwick and Constable § to produce six groups of protons, of which two are due to alpha particles of ranges between $3 \cdot 9$ and $3 \cdot 3$ cm. The authors give the alternative explanations of entry over the top or a broad resonance band. If we take the former as the explanation, then the height of the barrier is the energy of a $3 \cdot 3$ cm. range alpha particle, or $4 \cdot 6 \times 10^6$ electron volts. The two elements beryllium and boron have been investigated by Becker and Bothe ∥, who give curves for the yield of artificial gamma quanta against alpha particle energy :—Beryllium gives clear evidence of a resonance level at approximately $1 \cdot 4$ cm. alpha particle range, above which there is a flattening of yield at $1 \cdot 8$ cm. range, giving a barrier height of $3 \cdot 2 \times 10^6$ electron volts (their curve is substantially confirmed for the excitation of neutrons by Rasetti ¶). The curve for boron is not without uncertainty in interpretation, since there is some evidence of a resonance level at roughly

* Rutherford, Chadwick, and Ellis, 'Radiation from Radioactive Substances,' p. 297.

† E. Pollard, Proc. Roy. Soc. A. cxli. p. 375.

‡ H. C. Webster, Proc. Roy. Soc. A, cxxxvi. p. 444.

§ J. Chadwick and J. E. R. Constable, Proc. Roy. Soc. A, cxxxv. p. 54.

∥ H. Becker and H. Bothe, *Zeits. f. Phys.* lxxvi. p. 431.

¶ F. Rasetti, *Zeits. f. Phys.* lxxviii. p. 167.

the same value as for beryllium and no clear minimum to mark the true barrier height. Working on the neutron emitted from the same two elements Curie and Joliot * confirm the value for beryllium and give curves for boron which suggest a steady rise in yield after 1·93 cm. alpha particle range—or $3·3 \times 10^6$ electron volts. In the Bakerian Lecture for 1933 Chadwick † gives the values $3·5 \times 10^6$ e.v. for beryllium, $3·7 \times 10^6$ for boron, and $6·8$ to $6·9 \times 10^6$ for aluminium. These are systematically higher than those given here, which is probably due to the uncertainty in the precise meaning of the barrier height already mentioned.

There is indirect evidence for boron and nitrogen. If we assume that the tail at the end of the absorption curve of the protons liberated is due to their production by alpha particles whose energy varies from the maximum of the source to the height of the barrier, then substitution in the impact equations enables the height to be calculated. Energy and momentum considerations lead to the equation

$$2m_nQ = m_pv_p^2(m_p+m_n) - m_\alpha V^2(m_n-m_\alpha) - 2m_\alpha m_n v_\alpha v_p,$$

where the suffices refer to proton, nucleus and alpha particles and Q is the nuclear energy change. The value of Q can be calculated from the maximum range protons, which are produced by the full range alpha particles; the equations can then be used to find the minimum range alpha particles. This has been applied to nitrogen by Pollard ‡, and confirms the value found by direct methods. The proton absorption curves for boron have been found by Bothe §, and Chadwick, Constable, and Pollard ‖; these workers find long " tails " at the end of the two definite groups, as would be expected if the potential barrier were low. The values calculated from the long and short range groups are as follows :—

Bothe : $3·32 \times 10^6$ e.v.
                                                               $3·43 \times 10^6$ e.v.
Chadwick, Constable, and Pollard : $3·27 \times 10^6$ e.v.
                                                               $2·80 \times 10^6$ e.v.

* Irene Curie et F. Joliot, *Comptes Rendus*, cxcvi. p. 397.
† J. Chadwick, Bakerian Lecture, Proc. Roy. Soc. 1933.
‡ *Loc. cit.*
§ H. Bothe, *Zeits. f. Phys.* lxiii. p. 381.
‖ J. Chadwick, J. E. R. Constable, and E. Pollard, Proc. Roy. Soc. A, cxxx. p. 470.

The last value is doubtful, since the flattening at the top of the inside group cannot be estimated precisely. Taking the mean of the first three the value found is 3.34×10^6 e.v.

The experiments of Livingston and Lawrence * on disintegration by fast protons indicate that the effective nuclear cross-section reaches a constant value in the case of lithium at 300,000 volts, of aluminium 800,000 volts, with boron somewhat higher than lithium. They conclude that this critical energy is approximately proportional to the atomic number.

Evidence from Scattering Experiments.

There is difficulty in interpreting the results of alpha particle scattering experiments owing to the absence of a complete theory of such scattering. Thus, while the Born theory of collisions applied to a Coulomb field of force yields results which agree with experiment for low alpha particle energies, the influence of the field on the incident waves renders the theory invalid for closer collisions. This has been pointed out by Massey †, who shows how an approximate method can be used to give a value for the ratio of observed to classical scattering. He has not, however, carried out the numerical application.

It is not absolutely necessary to explain experimental results completely before making deductions as to the height of the barrier ; as has been indicated, the energy of an alpha particle corresponding to definite signs of anomalous scattering may be taken as a critical energy which can be compared with the critical energies found in disintegration. The most recent and most thorough experiments on the scattering of alpha particles are those of Riezler ‡. These show that while for collisions which are not very close the classical scattering law is obeyed, at high alpha particle energies the scattering becomes appreciably anomalous and the curves fit in with those calculated, assuming the partial waves of small order are affected by the transparency of the barrier. Thus for aluminium, alpha particles of 6.5 cm. range are found to give scattering which is markedly anomalous ; these particles have an angular momentum of $h/2$ if they are

* M. S. Livingston and E. O. Lawrence, Phys. Rev. xliii. p. 369.

† H. S. W. Massey, Proc. Roy. Soc. A, cxxxvii. p. 463 (1932).

‡ W. Riezler, Proc. Roy. Soc. A, cxxxiv. p. 168.

first order partial waves, and so approach to a distance of $6·0 \times 10^{-13}$ centimetres to have an appreciable change of entering the boron nucleus, which gives a critical height of $3·0 \times 10^6$ electron volts, in fair agreement with the previously deduced value, certainly within the experimental error. If in place of $4·8 \times 10^{-13}$ we had $4·5 \times 10^{-13}$, which would easily be possible, then the agreement would be exact. Riezler's results show that carbon has a distance of closest approach which is a few per cent. higher than boron, and beryllium one which is a few per cent. less. The value for boron found from the proton curves has been taken as correct, and the critical height for carbon estimated relative to it.

Riezler's results have been discussed numerically by Mukherjee *, who has extended Wentzel's calculation of the scattering by introducing an attractive force in addition to the Coulomb repulsion. He deduced values for the nuclear critical radii. As Massey points out, this theory does not take account of the perturbation of the incident alpha wave by the nuclear field, and so the radii are almost certainly too small in value. The interest in view of later discussion is that these radii (for Be, B, C) have approximately a constant value.

Collection of the Evidence.

We have, from minimum energy methods, the values for barrier heights to an alpha particle :—

Lithium	$2·8 \ \times 10^6$ electron volts.	
Beryllium	$3·14 \times 10^6$	,, ,,
Boron	$3·34 \times 10^6$	,, ,,
Nitrogen	$4·20 \times 10^6$	,, ,,
Fluorine	$4·65 \times 10^6$	,, ,,

From scattering experiments :—

Carbon ..... $3·6 \times 10^6$ (relative to boron).
Aluminium.. $6·16 \times 10^6$

Livingston and Lawrence † give the following figures for critical energies in disintegration by hydrogen ions.

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* K. K. Mukherjee, *Phys. Zeits.* p. 179.
† *Loc. cit.*

Above these energies the effective nuclear cross-section is constant.

Lithium ....   300,000 volts.
Boron ....   Somewhat higher.
Aluminium .....   800,000 volts.

These results are plotted against atomic number in the figure.   The upper line shows the heights to an alpha particle.   It will be seen that if allowance is made for
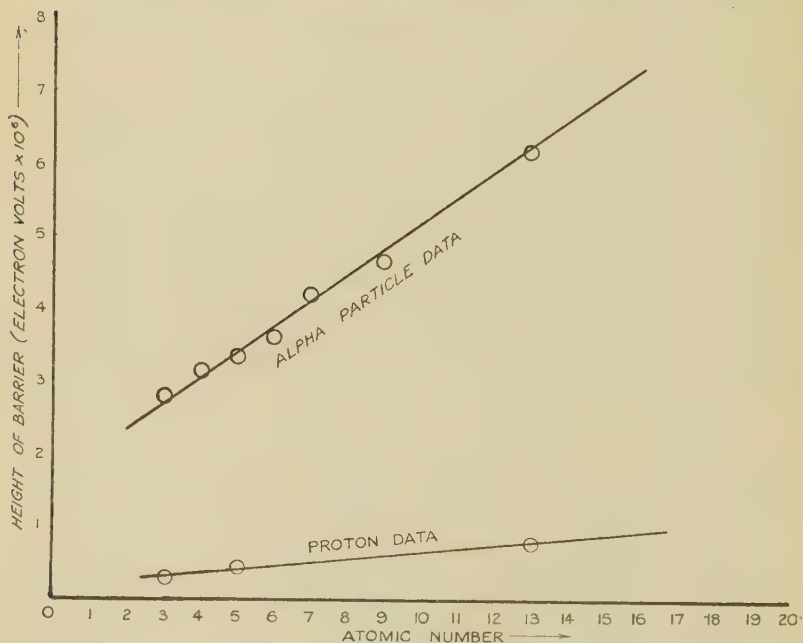
the experimental error a straight line relation holds which suggests the simple rule that *the height of a potential barrier is a linear function of the atomic number.*

The values given by Livingston and Lawrence are very much lower, but, as they point out, indicate that barrier height is proportional to atomic number.

If this simple rule is verified by later experimental work it is interesting for several reasons.   First, it shows that the disintegration of elements such as phosphorus and potassium must be due to the entry of alpha particles by resonance, since the barrier will be too high for entry

over the top ; second, it should give some information about the nature of the attractive force which is known to exist after a certain closeness of approach of the alpha particle ; third, it should be possible to explain it theoretically.

Discussion in the Light of Nuclear Theory.

Different suggestions have been put forward regarding the constitution of atomic nuclei in the past, involving protons, alpha particles, electrons, and neutrons, but our knowledge of the fundamental units has been, and still is, to a great extent too indefinite to render such suggestions other than speculative. In 1932 Heisenberg * published the first of a series of papers in which he developed a theory of the nucleus taking neutrons and protons only as his fundamental units of structure. He showed in particular how the stability of nuclei could be accounted for by supposing attractive forces $J(r)$, $K(r)$ between neutron-proton and neutron-neutron, together with the Coulomb repulsion between protons. An essential point of his theory is that the neutron-proton force, which is of the nature of a polarization attraction, exceeds the neutron-neutron force. A simple calculation on the basis of this theory shows that if, as is approximately the case, the number of neutrons is equal to that of the protons then the potential at the critical radius where repulsion balances attraction is proportional to the number of protons. The calculation is as follows :—

(For simplicity, neglect the neutron-neutron attraction, as it is less than the neutron-proton.) Suppose the neutron-proton attraction obeys a law of the form

$$\text{Potential} = A \cdot \frac{\text{no. of neutrons} \times \text{no. of protons} \times e^2}{r^p},$$

where r is the distance between neutron and proton and A is a constant. Let n_1 be the number of neutrons and n_2 the number of protons. Then the potential due to the Coulomb repulsion at a distance r will be (since the alpha particle has a charge $+2e$)

$$\frac{2n2e^2}{r},$$

* W. Heisenberg, *Zeits. f. Phys.* lxxvii. p. 1 ; lxxviii. p. 156 ; lxxx. p. 587.

while the attraction (since the alpha particle contains two neutrons and two protons) will be

$$\frac{2A(n_1+n_2)e^2}{r^p},$$

giving

$$V = \frac{2n_2 e^2}{r} - \frac{2A(n_1+n_2)e^2}{r^p}.$$

The critical radius occurs where the force is zero or dV/dr is zero, which gives the equation

$$r_c{}^{p-1} = \frac{pA(n_1+n_2)}{n_2}.$$

evaluating r_c, the critical radius. It can be seen that if $n_1=n_2$, r_c is constant, since p and A are supposed constant. This rather surprising result is not unexpected if it is remembered that the light elements in general differ from the preceding element by one proton and one neutron, so that the additional repulsive field is balanced by an equal attracting field. We then have for the critical potential

$$V_c = \frac{2n_2 e^2}{r_c}\left[1 - \frac{1}{p}\right],$$

V_c *is therefore a linear function of* n_2 *so long as* r_c *is constant.* The rule suggested by the experimental results is thus confirmed by this simple theory.

This will be true so long as $n_1=n_2$, and the actual structure of the nucleus does not need consideration. For very light nuclei, such as hydrogen or helium, this cannot be said, for heavier nuclei the approximation is more admissible. There is also the possibility of a distortion of the nucleus as a whole to be considered. Such distortion may have to be called on to explain the low energies of the incident protons in disintegration by hydrogen ions. Elements such as lithium, boron, or aluminium fall short of being entirely alpha particles by one proton ; in these elements the attraction between the odd neutrons and proton and the outside proton may be sufficient to detach these three and cause the breakdown of the whole nucleus into alpha particles. Such a suggestion is, however, entirely speculative.

The constancy of the critical radius must not be used to deduce that the light nuclei all have the same volume.

The volume of a nucleus, if it has any meaning, cannot be the volume of a sphere of radius r_c by the very nature of r_c, which is simply the distance of equilibrium between two kinds of forces due to particles further in.

It will be seen that the slope of the line relating V_c with n_2 determines the value of r_c providing the value of p, the index of the law of force, is known. If we assume that an inverse fifth-power law holds we can determine the critical radius of the light nuclei; calculation gives the value $5\cdot9 \times 10^{-13}$ cm. It is doubtful whether this method of deduction is valid for numerical calculation, so that the figure given may have very little meaning.

Summary.

The experimental evidence on the heights of nuclear potential barriers is collected and values found for seven light elements. It is shown that these values are a linear function of the corresponding atomic number. An explanation of this is suggested on the basis of Heisenberg's nuclear theory, and it is shown that a constancy of the critical radius of nuclei follows from the approximate equality in the numbers of neutrons and protons in the light elements, and that this accounts for the experimental rule.

XCVI. *The Quenching of Light from Flames produced by Various Chemicals.* By C. D. Child *, *Ph.D.*, *Professor of Physics, Colgate University* †.

Abstract.

When certain chemicals are added to solutions of calcium, strontium, sodium, and potassium salts which are being sprayed into non-luminous flames the amount of light

* Deceased July 15, 1933.
† Communicated by Prof. P. R. Gleason, Ph.D.

is in general diminished ; in a few cases it is increased. With calcium and strontium salts the amount of quenching varies greatly with the nature of the compound added ; with sodium and potassium the quenching is nearly the same in all cases.

These effects can be explained by assuming that the molecules are broken apart in the flame into atoms or groups of atoms which are continually dissociating and recombining. Apparently the equilibrium law holds when dissociation occurs in the flame.

Introduction.

THE addition of certain chemicals to salt solutions which are being sprayed into a " non-luminous " flame changes the amount of light given by the flames. The following is an account of this effect as shown by the red bands of calcium and of strontium and by the D-lines of sodium and the potassium lines 7668 and 7702 Å. These elements were chosen because the carriers which give the sodium and potassium lines absorb the same kind of light which they emit, while the carriers giving the calcium and strontium bands do not *.

The apparatus and the methods used in making these measurements were the same as those already described†, except that the relative candle powers of the flames were determined by replacing the photometer by two photronic cells arranged in the manner described by Gleason ‡. Measurements can be made by this method more accurately and quickly than with an ordinary photometer. These cells are also more sensitive in the red than is the eye.

When experimenting with calcium, strontium, and potassium, Eastman colour filters No. 26 were placed in front of the photronic cells. These do not transmit any appreciable light of wave-length shorter than 5900 Å. With sodium light, colour-filters No. 16 were used. These transmit no light of wave-length less than 5200 Å.

While making these measurements two sources of error were found to which attention had not previously been directed. The first of these was the erratic behaviour

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* Gouy, *Ann. de Chimie et Physique*, xviii. p. 45 (1879).
† Child, Phys. Rev. xxxviii. p. 699 (1931).
‡ Gleason, Rev. Scientific Instruments, iii. p. 556 (1932).

of the sprayers when the solution used is somewhat concentrated and the air that is being blown through the sprayers is under considerable pressure. In some cases it can be seen that a deposit forms on the inside of the nozzle B (see figure). When this occurs the amount of solution taken up by the air changes in a most erratic way. Thus with 1·8-N solution of NH_4Cl such a deposit was formed, although a saturated solution of this salt contains more than twice the amount of NH_4Cl that was being used.

Moreover, even when there was no visible deposit of salt in the nozzle the action of the sprayer became erratic with concentrated solutions. Thus with a 2-N solution of NaCl and a pressure of the air of more than 10 cm. of mercury, the candle power of the flame into which the
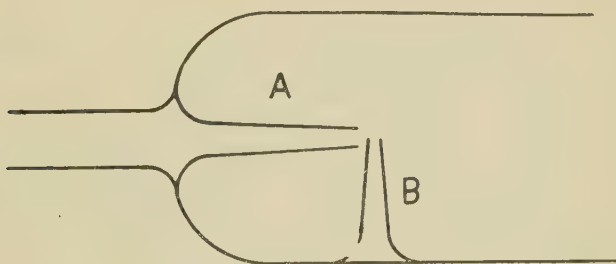
Arrangement of nozzles in sprayer.

spray was sent often varied as much as 10 per cent. within a few seconds.

If any salt was left from previous use of the sprayer, or if any lime from tap water dried on the nozzle of the sprayer, the luminosity of the flame varied more than when the sprayer had been properly cleaned. Some sprayers gave more erratic results than others which were identical in appearance.

It was also found that the ratio between the candle powers of two flames into which solutions of different concentrations were being sprayed increased somewhat as the pressure of the air blown throuhg them was increased. For example, the ratio between the light given by a 2-N solution of NaCl and that given by a 0·2 N solution increased 20 per cent. when the pressure of the air was increased from 5 cm. to 25 cm. of mercury.

The following is suggested as a possible explanation
for this behaviour.   When air is blown through the
nozzle of the sprayer A (see figure) the solution is drawn
to the top of B.   There it is partly vaporized and partly
broken up into fine particles which are carried to the
flames.   If the solution is near the saturation point, the
vaporization causes particles of salt to form at the top
of B.   These clog the opening and cause the amount of
spray to vary.

If the solution is not saturated, there is still a rapid
vaporization in B, and the solution there becomes at
times more concentrated than elsewhere.   Consequently,
the strength of the solution blown into the flame varies.
Naturally, the nearer the solution is to the saturation
point the more irregular the amount of light given by
the flames.

Again, when the flow of air through the sprayer is less
there is less vaporization and consequently less variation
in the character of the spray.

Attention may also be called to the fact, when making
measurements, that the ratio between the candle powers
of flames into which different concentrations of salts
are being sprayed depends on the size of the flames, as
has already been shown *.   The same thing is true
when flames containing spray from different solutions are
compared.

It was thought at one time that the exceptional results
obtained when $NH_4C_2H_3O_2$ was added to NaCl and to
KCl and when NH_4Cl was added to $Ca(NO_3)_2$ might be
due to a difference in the amount of spray obtained from
different solutions under the same conditions.   This was
tested by weighing the sprayer and the solution before
and after air had been blown through the sprayer for
five minutes.   While the results obtained by such
weighings were not altogether consistent, as far as could be
determined the amount of spray was the same for all
solutions.

Effect of adding different Salts to the Solutions sprayed into the Flames.

There are given in Table I. the relative candle
powers obtained when various compounds were added

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* Child, Phys. Rev. xxxviii. p. 703 (1931).

to 0·2-N solutions of calcium, strontium, sodium, and potassium salts and the resulting mixtures sprayed into the flames. At the top of the table are given the solutions to which the various compounds were added. In the first column are given the various compounds added. Sufficient amounts of these were used to make 1·8-N solutions of the added compounds. For example, to a solution containing 0·2-N $CaCl_2$ sufficient NH_4Cl was added to make a 1·8-N solution of the latter, so that it contained ten times as much chlorine as did the original solution of $CaCl_2$. The columns after the first give the relative candle powers obtained from the solutions. In each column the candle power obtained from the solution without any added compound was taken as one.

TABLE I.

	$CaCl_2$.	$SrCl_2$.	$Ca(NO_3)_2$.	$Sr(NO_3)_2$.	NaCl.	KCl.
	1·00	1·00	1·00	1·00	1·00	1·00
$NH_4C_2H_3O_2$.	0·84	0·88	1·06	0·96	0·92	0·90
HCl	0·71	0·74	1·08	0·92	0·85	0·83
NH_4Cl	0·74	0·73	1·55	1·09	0·85	0·83
$CdCl_2$	0·77	0·77	1·15	0·90	0·86	0·82
Al_2Cl_6	0·09	0·12	0·15	0·12	0·85	0·83
HNO_3	0·38	0·50	0·82	0·76	0·85	0·87
NH_4NO_3 . . .	0·34	0·46	0·78	0·74	0·85	0·85
$Al(NO_3)_3$ . . .	0·03	0·035	0·04	0·04	0·85	0·85

Because of the various sources of error which have been mentioned data somewhat different from those given above will no doubt be obtained when either the conditions of the experiment or the kind of apparatus are varied, but several repetitions of these measurements show that the values given are very approximately correct for the condition under which the experiment was performed.

There is shown in Table II. the quenching effect produced when different amounts of $Al(NO_3)_3$ were added to a 0·2-N solution of $SrCl_2$. Column 1 gives the amount of $Al(NO_3)_3$ added to the solution, the unit being the amount necessary to make a normal solution of that salt. Column 2 gives the relative candle power of the flames into which the solutions were sprayed.

The amount of light given by $SrCl_2$ solutions of different concentrations is shown in Table III. Column 1 gives the strength of the solution used, a normal solution being taken as the unit. Column 2 gives the relative candle power. Column 3 gives the ratios between the values given in Columns 2 and 1, that is, the candle power per unit of $SrCl_2$ for different concentrations.

TABLE II.

$Al(NO_3)_3$ added.	Relative candle power.
0·0	1·0
0·2	0·47
0·4	0·22
0·6	0·13
0·8	0·08
1·2	0·043
1·6	0·03

TABLE III.

Strength of solution.	Relative candle power.	Candle power per unit of $SrCl_2$.
4·0	1·00	0·25
3·2	0·89	0·278
2·4	0·78	0·325
1·6	0·61	0·38
0·8	0·42	0·52
0·5	0·25	0·63
0·2	0·15	0·75

The most obvious fact shown by Table I. is the difference between the reactions to the added compounds of the strontium and calcium flames on the one hand and those of the sodium and potassium on the other. In the former case the different added compounds produce distinctly different results, while with the latter the effects are nearly the same in all cases. The only exception to this statement occurs when $NH_4C_2H_3O_2$ is added to solutions of sodium and potassium salts. The reason for this exception is not at present apparent.

The data for the alkali earth flames may be summarized as follows. First the effect which the added chemical has depends both on its acid and on its base radical. Thus both Al_2Cl_6 and HNO_3 quench the light much more than does HCl, the Al_2Cl_6 because of the difference in its base and the HNO_3 because of the difference in the acid part.

Secondly, the addition of a nitrate quenches the light more than that of the corresponding chloride. Thus HCl quenches the light from $SrCl_2$ 23 per cent., while HNO_3 quenches it 47 per cent.

Third, in general the addition of a compound diminishes the candle power of the light given by the original solution. However, in five cases the addition of a chloride to a nitrate increases the candle power.

Explanation of Data.

At least a qualitative explanation of the preceding data can be given by assuming that the molecules in the flames are continually dissociating into two or more atoms or groups of atoms and again recombining, as in a water solution *. Whether the molecules dissociate directly into uncharged atoms, or into charged ions which quickly change to uncharged atoms, cannot at present be stated, but certainly the sodium and potassium lines which are here studied are produced by excited and not by charged ions. The same is, no doubt, true of the carriers giving the band spectra of calcium and strontium.

Thus NaCl is dissociated into sodium and chlorine, and increasing the number of chlorine atoms increases the chance of a sodium atom combining with a chlorine atom. Such combination diminishes the number of uncombined sodium atoms and consequently the amount of sodium light obtained per unit weight of sodium salt sprayed into the flame. This occurs whether the increased number of chlorine atoms is due to the addition of more NaCl or to some other chloride. In other words, we are assuming that the equilibrium law applies here as with water solutions.

It is commonly assumed that the calcium and strontium bands which are here studied are due to calcium and

* Child, Phys. Rev. xxxviii. p. 705 (1931).

strontium oxide respectively. If so, it is reasonable to assume that when $CaCl_2$, for example, is sprayed into a flame it is dissociated, so that at times the calcium atom is uncombined and at such times gives the calcium line 4226 Å. ; part of the time the calcium atom is combined with oxygen and gives the calcium oxide spectrum ; and part of the time it is combined with chlorine and gives no spectrum in the flame. The more chlorine there is present in the flame the oftener the calcium atom combines with the chlorine and less light comes from the calcium atom and also from the calcium oxide group This would explain the quenching effect of the chlorine on the bands, and would also correspond with the fact observed by Gouy * that the light from the calcium line is proportional to that from the calcium band, both when the concentration of the solution and when the character of the acid radical is changed.

Thus a 4-N solution of $CaCl_2$ gives four times as much light as a 0·4-N solution instead of ten times as much, which it would give if the amount of dissociation were not diminished by the increased amount of chlorine present. Again increasing the amount of chlorine by adding HCl to the $CaCl_2$ solution diminishes the amount of light 29 per cent., although the amount of calcium present is not in any way diminished.

Moreover, it is not unreasonable to assume that some of the added compounds are dissociated in the flame more than others, so that they set free more chlorine atoms. These may combine with the calcium atoms, so that fewer of the molecules which give the calcium band are present, and consequently there is a greater quenching effect. Thus Al_2Cl_6 no doubt dissociates in the flame to a much greater extent than does HCl, and consequently quenches the light more than does HCl. The relative amount of dissociation of these compounds is evidently quite different in flames from what it is in water.

This view is also in harmony with the fact that those acid radicals occurring in the compounds which give the less light also have the greater quenching effect. Thus Gouy found only 66 per cent. as much light given by $Ca(NO_3)_2$ as by $CaCl_2$†. The corresponding ratio found

* Gouy, *Ann. de Chimie et Physique,* xviii. p. 95 (1879).
† *Loc. cit.*

with the apparatus used in this work was 43 per cent. Corresponding to this is the fact that a nitrate added to $CaCl_2$ has a greater quenching effect than does the corresponding chloride. Apparently the NO_3 radical when in the flame has a greater affinity for calcium than does chlorine, so that $Ca(NO_3)_2$ does not dissociate as much as does $CaCl_2$ and consequently gives less light. Similarly, when a nitrate is added to a solution of $CaCl_2$ the NO_3 radical combines with the calcium in the flame and thus diminishes the number of molecules giving the band spectrum of calcium.

The assumptions here made also explain the increase in luminosity produced by adding HCl to a solution of $Ca(NO_3)_2$. When this is done HNO_3 is formed, and this being but slightly dissociated causes a decrease in the concentration of NO_3. This action is followed by a further dissociation of $Ca(NO_3)_2$ and an increase in the number of calcium atoms and of the calcium oxide molecules which give the bands.

When CCl_4 is blown into a flame the sodium light coming from the flame is quenched to a very large extent *. This is no doubt due to the oxidation in the flame of the carbon setting free the chloride atoms. These combine with the sodium present with a decrease in the number of sodium atoms and the light coming from them.

Attention may also be called to the fact that the candle power given by solutions of $SrCl_2$ of different concentrations as shown in Table III. varies, as would be expected, if the $SrCl_2$ molecules are dissociated into two parts which obey the equilibrium law, and from one of which the band spectrum is obtained.

Some further statement is needed to explain the action of the alkali metal salts. The light from such salts is quenched to nearly the same extent by all of the added compounds. This is in harmony with the results of Gouy, who found that the light given by different compounds of sodium and potassium was independent of the acid radical †.

It was suggested by Arrhenius ‡ that after the alkali metal salts are dissociated in the flame, the metal atoms combine with OH radicals, so that their behaviour in

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* Franck and Gibson, *Zeits. f. Phys.* l. p. 691 (1928).
† Gouy, *Ann. de Chimie et Physique*, xviii. p. 95 (1879).
‡ Arrhenius, *Wied. Ann.* xlii. p. 40 (1891).

the flame is the same as that of the hydroxide, irrespective of the nature of the compound originally sprayed into it.

This is much the same as the assumption that the calcium and strontium combine in the flame to form calcium and strontium oxide. There is, however, the difference that the atoms of the alkali earths must be thought of as dissociating and recombining at times with the oxygen, and at other times with the acid radicals present in the flame, and consequently the number of atoms combining with the oxygen is influenced very appreciably by the kind of acid radical present. On the other hand, the atoms of the alkali metals must be thought of as dissociating and recombining almost entirely with the OH radical and scarcely at all with the acid radical, so that the number so combining is little affected by the kind of acid radical.

The writer desires to express his appreciation for suggestions concerning this work that have been given him by Professors A. E. Wood and P. R. Gleason of Colgate University.

Note added in proof.—It is regretted that the death of Dr. Child prevents further contributions from him on problems related to the subject of this paper. He did not include in this paper some results he had obtained in a preliminary way, for he planned to study them further before reporting them. Spectrograms taken of a carbon arc impregnated with salts of calcium show that the red bands are somewhat different for $CaCl_2$ than for $Ca(NO_3)_2$. It is probable that an extended study of such factors would yield a more complete explanation of the data of Table I.—P. R. G.

XCVII *Notices respecting New Books.*

Actualités Scientifiques et Industrielles.
Hermann et Cie, Paris.

No. 42. *Conséquences de la rélativité dans le développement de la mécanique ondulatoire.* By Louis de Broglie. [Pp. 14.] (1932. Prix 6 fr.)

The relativistic consequences of treating radiation as corpuscular, the corpuscles having a velocity approaching c

and a mass approaching zero, are briefly discussed, and also the consequences of associating a vibratory frequency with a moving particle. The bearing of the results on the development of wave mechanics is indicated.

No. 49. *La philosophie scientifique.* By HANS REICHENBACH. [Pp. 43.] (1932. Prix 10 fr.)

This brief survey, a translation of ' Ziele und Wege der heutigen Naturphilosophie,' is of considerable interest as giving the outlook of a new and active school of scientific philosophers. Philosophical discussion is based on the analysis of scientific knowledge as it now is, rather than on abstract speculation, pure thought, or the analysis of " reason." Much of the traditional theory of knowledge is criticized as being necessarily inadequate, as it is based on a conception of the world which is now superseded. A number of problems of biopsychology, physics, and mathematics, and concerned with reality and free will are briefly discussed ; a central element is the acceptance of experience as the basis for pronouncements on the real, rather than *a priori* judgments.

No. 50. *Les bandes moléculaires dans les spectres stellaires.* By P. SWINGS. [Pp. 29.] (1932. Prix 7 fr.)

An excellent summary is given of present knowledge of the molecular spectra of stars. Molecular bands are very sensitive to temperature and pressure conditions. In view of various anomalies in the association of some of the molecular bands with particular stellar types the technical precautions necessary in the spectrographic investigations are emphasized. The need for a more systematic quantitative study of the bands of the colder stars is pointed out.

No. 51. *Structures et propriétés optiques des carbonates.* By H. BRASSEUR. [Pp. 29.] (1932. Prix 7 fr.)

Work on the relation of the optical properties to the crystal structure of carbonates, particularly that of Bragg, is reviewed. From the known optical properties of carbonates of unknown structure predictions are then made as to the positions of the CO_3 groups. Crystals with groups similar to CO_3 are also briefly discussed.

No. 58. *La recherche scientifique.* By J. PERRIN. [Pp. 24.] (1933. Prix 6 fr.)

After sketching in broad outline the course of development of the human race from pre-historical times Perrin emphasizes the rapidity of the changes of conditions which have been associated with the rise of scientific research. The essential qualities of the research worker differ from those of the savant

or the inventor. An urgent plea is put forward for the ade-
quate support of disinterested research to accelerate progress
towards the " free and happy city " of the future.

No. 59. *La diffraction de la lumière par des ultra-sons.* By.
L. Brillouin. [Pp. 32.] (1933. Prix 10 fr.)

Following up earlier work Brillouin gives a detailed mathe-
matical investigation of the propagation of electromagnetic
waves through a medium in which elastic vibrations are
occurring. The theory is applicable to the diffraction of light-
waves in a liquid or solid medium, in which the vibration is
controlled by a quartz oscillator. Conditions analogous
to those of Bragg for selective reflexion are found. The
experimental work, which gives results verifying the theory,
is briefly described. It is interesting to note that the theory
is similar to that involved in the treatment of the interaction
of electronic and elastic solid waves in the theory of electric
conductivity.

No. 63. *L'univers en expansion.* By H. Mineur. [Pp. 41.]
(1933. Prix 12 fr.)

The characteristics of the Einstein and de Sitter universes
are indicated, and are shown to be incompatible with the
observational results on the recession of nebulæ. The solutions
of the equations, due to Friedmann, Lemaître, and de Sitter,
corresponding to a variable radius, are then discussed, and
an account is given of Eddington's calculation of the cosmical
constant. The succinct lucidity of the presentation will be
appreciated by those who have a general familiarity with the
usual mathematical treatment of general relativity.

No. 68. *Réel et déterminisme dans la physique quantique.*
By E. Meyerson. [Pp. 49.] (1933. Prix 10 fr.)

Science aims, in Meyerson's view, at explanation in terms
of objects having the essential characteristic of permanence.
Success in explanation, in reducing phenomena to a causal
scheme (causality being a form of logical identity) is inevitably
incomplete ; basic irrational elements occur in any scheme.
A striking feature of quantum physics may then be expressed
by the statement that the basic irrationality is characterized
by indeterminacy. The argument is largely in the form of
a criticism of views as to the significance of quantum physics
put forward by Planck, Bohr, Heisenberg, and others. The
penetrating criticism of the attempts to reduce free will to
quantum indeterminacy is particularly valuable. This essay
forms an excellent introduction to Meyerson's larger works.

*[The Editors do not hold themselves responsible for the
views expressed by their correspondents.]*

Fig. 2.
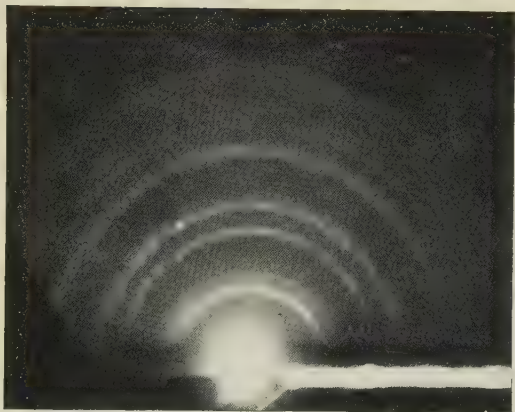
Silver showing recrystallization.

Fig. 3.
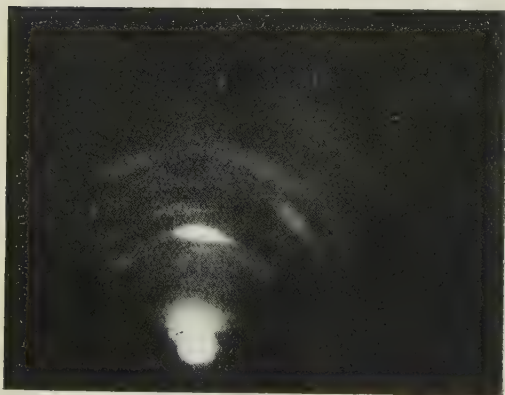
Zinc showing (101) orientation.

Fig. 4.
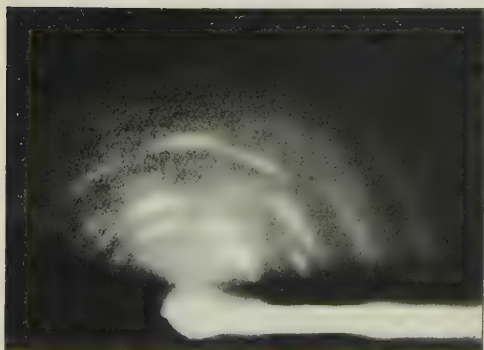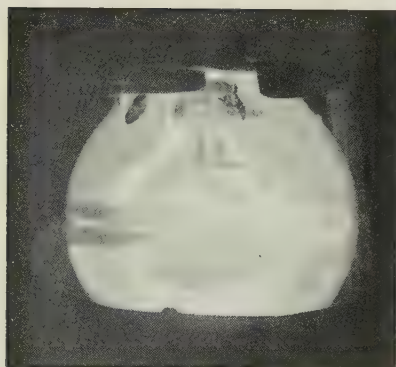
a.
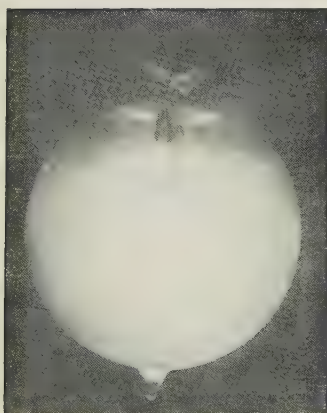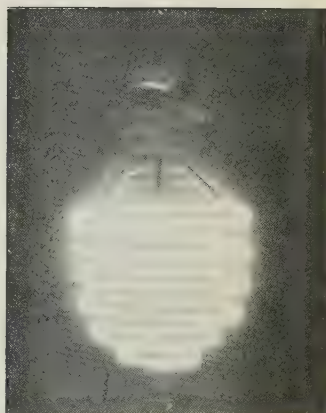
b.   *c.*

a. **Argon** lamp glowing and electric current passing through electrolytic bath and bulb.

b. **Sodium glow** in lamp.

c. **Argon glow** (no sodium in bulb).
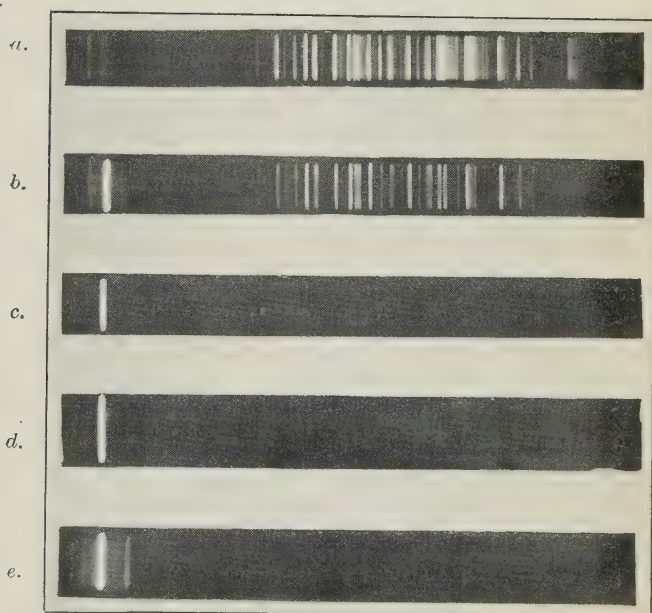
a. Spectrogram of argon glow.

b. Spectrogram of sodium-argon glow near electrodes (bulb not heated).

c. Spectrogram of sodium-argon glow away from electrodes (bulb not heated).

d. Spectrogram of sodium-argon glow (bulb heated).

e. Spectrogram of sodium-argon glow (current passing through electrolytic bath and bulb).

INDEX to VOL. XVI.

END OF THE SIXTEENTH VOLUME.